july 1959

# nlgi spokesman

journal of the national lubricating grease institute

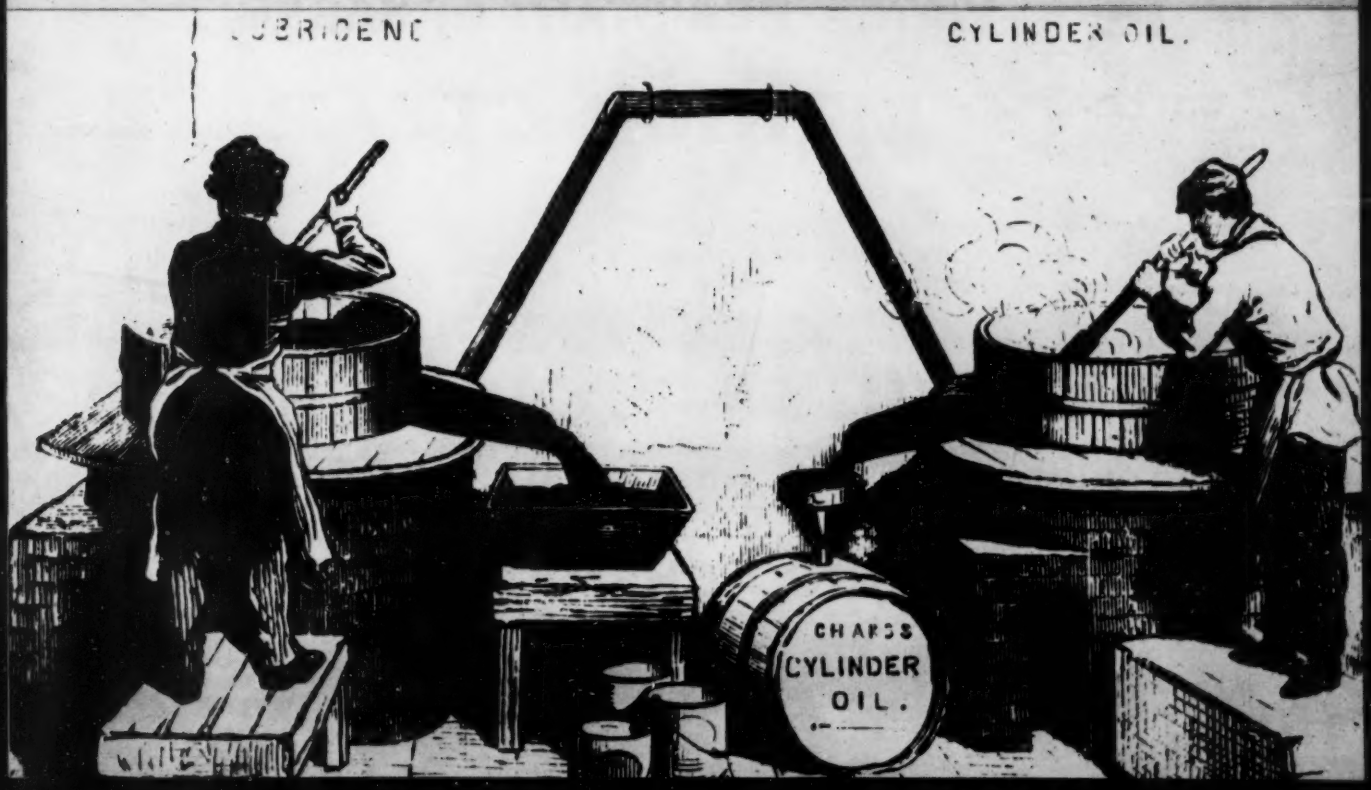
## Flow Mechanism of Thixotropic Substances

By S. J. HAHN, T. REE and H. EYRING

## The Analysis of Fatty Acid Esters by Gas Chromatography

By N. BRENNER, P. R. SCHOLLY and L. O'BRIEN

## Oil's First Century



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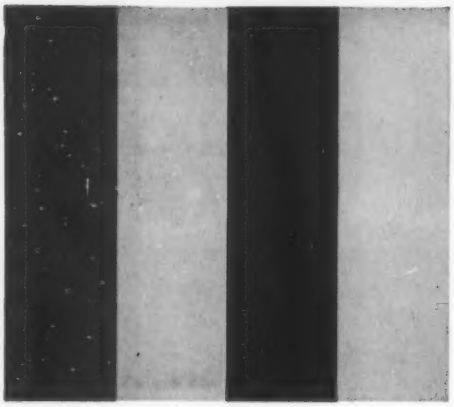


## NLGI PRESIDENT'S PAGE

By F. E. ROSENSTIEHL, *President*

# Another Look at the Chassis Lubrication Problem

Under the auspices of the API Lubrication Committee, an independent survey was recently made to determine new car dealers' attitudes toward oil change and chassis lubrication. The survey was conducted among two thousand new car dealers statistically selected on a nation-wide basis. While considerable publicity has been given the oil change portion of the survey, very little mention has been made regarding chassis lubrication.

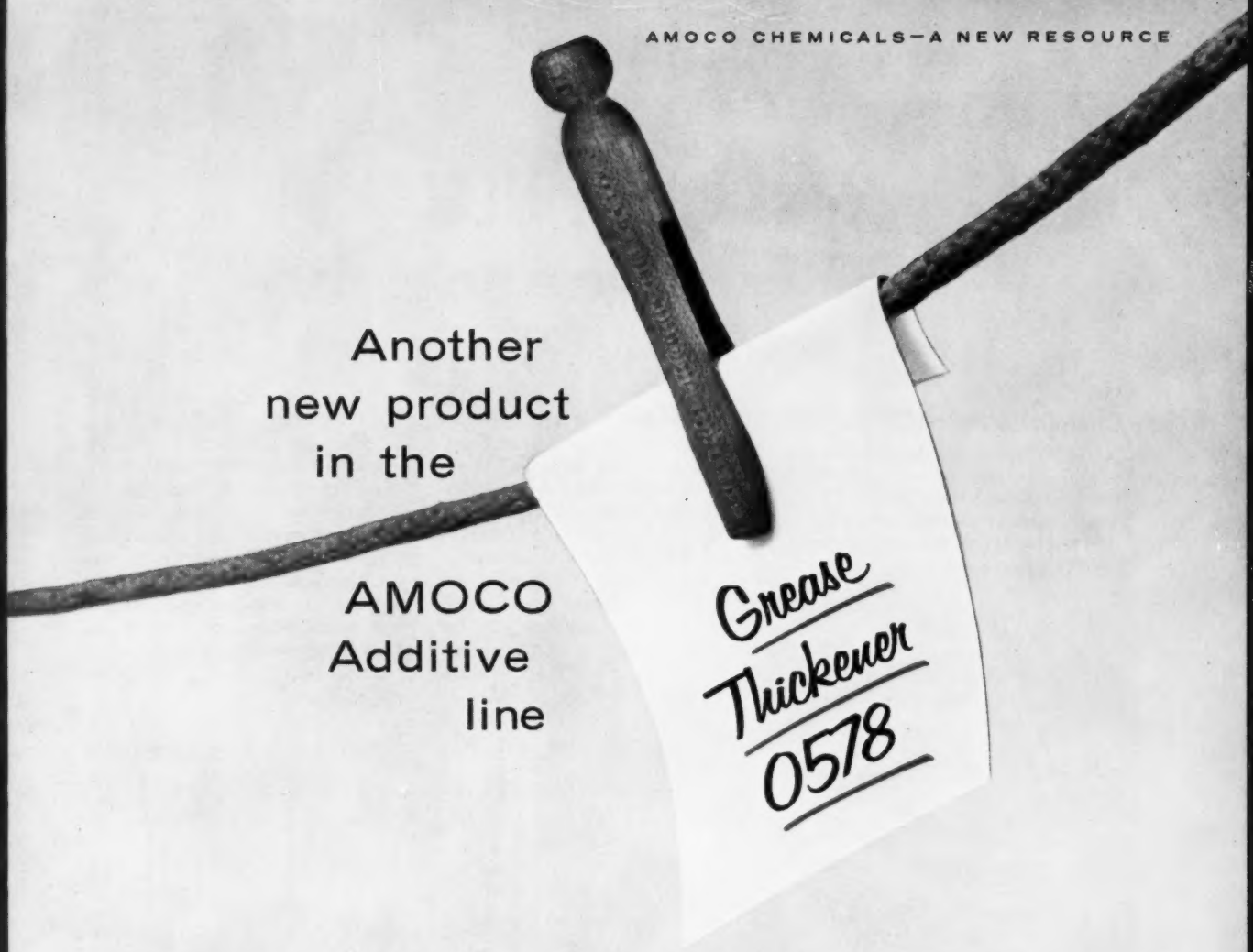
Briefly, the survey reveals 84.6 per cent of the dealers contacted feel chassis lubrication is an important factor in securing the customer's other service business. Further, 96.9 per cent of the dealers recommend to their customers some definite interval for chassis lubrication. Of these, 80 per cent recommended 1,000 miles, 9 per cent 1,500 miles and 9.5 per cent 2,000 miles.

An interesting facet of the survey is the fact that 98.2 per cent of the dealers feel chassis lubrication often reveals unsafe conditions. The vast majority of these have themselves actually had experiences where unsafe car conditions were found while lubricating the chassis.

The above again confirms what has frequently been stressed by NLGI in the past, that the 1,000 mile interval is the proper one for chassis lubrication. Not the least of the reasons for this frequent and regular chassis lubrication is the fact that unsafe conditions are often found in the process

If the grease industry is to offset the declining market in automotive greases—due largely to the steady reduction in the number of chassis grease fittings themselves—then one thing we must do is to publicize as widely as possible such sound and objective studies as this one sponsored by the API. The public acceptance and practice of more frequent chassis lubrication is of course no final solution to the problem posed by the reduction—and perhaps even elimination—of car grease fittings. But a successful campaign *can* provide the industry with an effective buffer to ease the marketing problem while other areas of grease lubrication are developed and opened up to absorb the loss in the automotive field.

AMOCO CHEMICALS—A NEW RESOURCE




# Another new product in the AMOCO Additive line

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A dropping point of 480° F. is typical for No. 2 greases formulated with Amoco's new Grease Thickener 0578.

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# News About NLGI

## Chemico Joins NLGI

Chemico, Ltd. of Johannesburg, South Africa, is the newest member firm to affiliate with NLGI. The new Technical member will be represented by Mr. O. Richter, managing director, as Company Representative, while Dr. H. Friede, chief chemist, will assist as Technical Representative.

## Pohorilla Conducts Survey

All Technical Representatives of NLGI are being questioned as to their attitudes on incompatibility between greases, prior to planning a program by the Technical Committee to educate consumers of the problems created by these factors which face lubricating grease marketers:

1. Incompatibility between different types of greases is known to be a deteriorating element with regard to performance;
2. The lubricating grease industry is marketing many new types of greases as compared to a decade ago, which has intensified the likelihood that mixing of greases will occur.

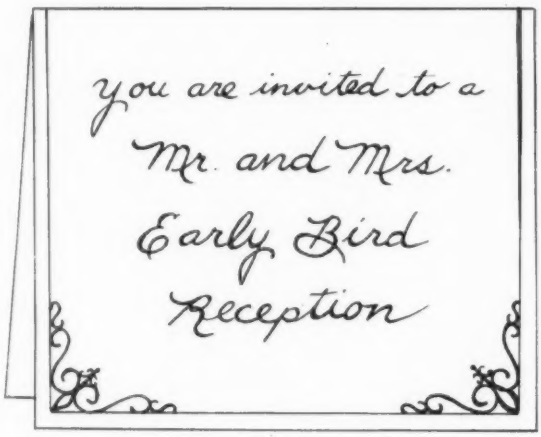
M. J. Pohorilla, vice-chairman of the Technical Committee, is conducting the survey. Questionnaires, mailed in early June, are to be returned to him at the Kendall Refining company in Bradford, Penna., by July 10.

## New NLGI Booklet

The famous NLGI booklet on lubrication on front wheel bearings is about to be joined by another intra-industry effort, entitled "Recommended Practices for Lubricating Passenger Car Ball Joint Front Suspensions." The ball joint booklet is nearing the final stages of approval, after matriculating through technical and marketing committees of NLGI. The final considerations are currently being given by a committee chairmanned by W. M. Murray, Kerr-McGee Oil Industries. Working with Murray are S. C. M. Ambler of British American Oil, F. R. Hart of Standard Oil (California), W. A. Magie, II of Magie Brothers Oil, G. E. Merkle of Fiske Brothers Refining, and F. T. Shaffer of Shell Oil.

Once final approval is received, the booklet will be printed and offered to NLGI members at cost. As was done with the wheel bearing manual, the ball joint manual will be available for company imprint. Distribution of the wheel bearing manual has exceeded 130,000 copies.

## Innovations at Next Annual Meeting




A new development for the NLGI Annual Meeting in New Orleans next October will be a special program for the wives of members. Because of the many scenic and historic sights in the famous Crescent City, a large number of the ladies are expected to attend.

Acting as hostess for the NLGI ladies will be Mrs. W. H. Saunders, Jr., with co-hostesses Mrs. B. G. Symon and Mrs. H. M. Fraser, all of New Orleans. Tours of the Vieux Carré and the Garden District are planned, with luncheons at historic restaurants, during the daytime Annual Meeting sessions.

Evening activities will include a "Mr. and Mrs. Early Bird Reception" on Sunday, October 25, as well as the traditional Annual Banquet, preceded by a social hour.

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# Future Meetings

**JUNE, 1959**

1-5 Fifth World Petroleum Congress Exposition, The Coliseum, New York City.

8-9 Petroleum Packaging Committee Meeting, Cleveland Ohio.

14-19 SAE Summer Meeting, Chalfonte-Haddon Hall, Atlantic City, N. J.

21-26 ASTM Annual Meeting Chalfonte-Haddon Hall, Atlantic City, N. J.

**AUGUST, 1959**

16-21 1959, National Congress of Petroleum Retailers Inc., 13th Annual Session, Jung Hotel, New Orleans, La.

**SEPTEMBER, 1959**

14 NLGI Board of Directors Meeting, Hotel Roosevelt, New York City.

16-17 Ohio Petroleum Marketers Association, Fall Conference and Golf Tournament, Sheraton-Cleveland Hotel and Lakewood Country Club, Cleveland, Ohio.

16-18 NPA Annual Meeting, Hotel Traymore, Atlantic City, N.J.

27-29 IOCA 12th Annual Meeting, Pick-Congress Hotel, Chicago, Ill.

**OCTOBER, 1959**

2-3 Association of Desk and Derrick Clubs of North America, 8th Annual Convention, Hilton Hotel, San Antonio, Tex.

11-15 ASTM Committee D-2 Meeting, Sheraton - Palace Hotel, San Francisco.

12-13 Petroleum Packaging Committee Meeting, Port Arthur, Texas

19-21 ASLE and ASME Joint Lubrication Conference, Sheraton-McAlpine Hotel, New York City.

**26-28 NLGI Annual Meeting, Roosevelt Hotel, New Orleans, La.**

28-30 Society of Automotive Engineers, National Fuels and Lubricants, La Salle Hotel, Chicago.

**NOVEMBER, 1959**

9-11 API, 39th Annual Meeting, Conrad Hilton, Palmer House and Congress Hotels, Chicago.

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# nlgi spokesman

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## THE COVER

WITH the celebration of Oil's first century, based on the anniversary observance of the Drake well, the lubricating grease industry may well pause to observe its own progress. Working with tallow and fats, or as shown on our cover, cooking oil, one batch at a time to process a lubricant, was a tiresome procedure . . . a far cry from the modern and complex products blended by the industry one hundred years later. Along with the technical progress is the growth of a thought concept—that proper lubrication is an excellent way to insure preventative maintenance. Story on p. 143.

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# ANNUAL MEETING, 1959

## Tentative Titles, NLGI 27th Annual Meeting Roosevelt Hotel, New Orleans, October 25-28

A steady growth pattern in the Institute's yearly meeting has introduced two new activities . . . the "Mr. and Mrs. Early Bird Reception" (see below) and the planned tours for wives. The reception will be held on Sunday evening, prior to the opening of the meeting. Titles listed below are tentative and will be confirmed in later issues of the journal, when speakers will also be listed. H. A. Mayor, Jr. (Southwest Grease) is chairman of the program committee, assisted by E. W. Campbell (Gulf), T. W. Binford (D-A Lubricants), W. A. Magie, II (Magie Brothers), Dr. J. V. Starr (Esso), T. A. Maxwell (Delta) and J. Y. McCollister (McCollister Grease).

*Sunday, October 25*
"Mr. and Mrs. Early Bird Reception"

*Monday, October 26* (morning session)
Address of Welcome
Keynote Speaker
Ten Years in Retrospect

*Monday, October 26* (afternoon)
SPOTLIGHTING THE CHASSIS LUBRICANT MARKET
a. Current Status of the Non-Lubricated, Non-Metallic Bearing in the Automotive Industry
b. Procedures for Testing and Evaluating Chassis Lubricants
c. Interpretation of Transit Authority Chassis Lubricant Test Data
A Marketing Paper

ANNUAL BUSINESS MEETING

*Tuesday, October 27* (morning session)
GENERAL
The Latin American and European Grease Manufacturing Industries
A Modified Clay Thickener for Lubricating Fluids
A Study of Open Gear Lubrication
A Comprehensive Review of Lubricating Grease Containers
Retention of Liquids in Soap/Hydrocarbon Systems

*Tuesday, October 27* (afternoon)

SESSION A
SPOTLIGHTING MANUFACTURING PROCEDURES AND EQUIPMENT
1. Grease Mixer Design
2. New Procedures for Gelling Synthetic Fluids
3. A Philosophy of Grease Milling
4. To Be Announced
5. A New Technique for Measuring Grease Consistency in the Mixer

SESSION B
SPOTLIGHTING OUR DISPENSING PROBLEMS
(Papers to be announced in succeeding issues of the NLGI SPOKESMAN)

ANNUAL SOCIAL HOUR

ANNUAL BANQUET

*Wednesday, October 28* (morning session)
TECHNICAL COMMITTEE MEETING
Reports of Committees

### The Ladies Are Invited . . .

Scenic New Orleans means a different type of Annual Meeting, with many wives attending, and sightseeing on the agenda. The Institute will announce plans for ladies' entertainment and social activities at a later date, but all couples are cordially invited to attend the "Mr. and Mrs. Early Bird Reception" at the Roosevelt Hotel in New Orleans, Sunday Evening, October 25.

Sponsored by more than twenty NLGI Associate member firms, "Early Birds" may meet old friends and gain new ones at the reception. This congenial get-acquainted affair will be the first formal part of the Annual Meeting . . . Sunday evening, 6 to 7:30 p.m.

By: S. J. Hahn
T. Ree
H. Eyring
University of Utah

Fundamental Research—4

SHOWN lecturing at the 26th Annual Meeting, Dr. H. Eyring

# Flow Mechanism of Thixotropic Substances

**Abstract**

In a thixotropic system, there are two kinds of molecules, entangled and disentangled. Entangled molecules make a three-dimensional network, in which disentangled and solvent molecules are enclosed. The entangled molecule, whose flow behavior is non-Newtonian, transforms to the disentangled molecule of Newtonian character as a result of stress. If the stress is relieved, the transformed molecule returns to its original state only after marked delay. Using this model, two flow equations are derived: One equation is applied to the "upcurve" which is obtained by measuring rates of shear with increasing stress, whereas the other is applied to the "downcurve," the flow curve in the reserve direction of the upcurve. The authors' theory is applied to silicone oil, printing inks, shaving cream, heavy mineral oil, grease and mayonnaise with good agreement with experiment.

## I. Introduction

Thixotropy is a very common phenomenon and is important in the paint, printing ink, and food industries. Many interesting observations on thixotropy have been reported in books[12, 15, 18, 41] as well as in papers[7, 19, 20, 25, 28, 42, 43, 44, 47, 48] and the mechanisms have been frequently discussed by various investigators.[1, 6, 7, 17, 18, 19, 26] However, no satisfactory theory has been proposed which explains thixotropy quantitatively.

Thixotropy is defined here as the phenomenon having the following characteristics: (1) It accompanies an *isothermal* structural change which is brought about by applying mechanical disturbance to a system; (2)

When the mechanical disturbance is removed, the system recovers its original structure; (3) The flow curve (shear rate versus shear stress) of the system has a hysteresis loop. This definition accords with that accepted currently,[12,18,41] although some investigators still include in thixotropy other phenomena.

## II. The Proposed Theory

### 1. *Flow Equation for a Non-Thixotropic System*

The flow equation of a system, which contains Newtonian and non-Newtonian units, is represented by[36,37,38,39]

$$f = \frac{x_1\beta_1}{\alpha_1}\,\dot{s} + \frac{x_2}{\alpha_2}\sinh^{-1}\beta_2\dot{s} \qquad (1)$$

Here f is stress, $\dot{s}$, rate of shear,

$$\alpha_i = (\lambda\lambda_2\lambda_3)_i/2kT \qquad (2)$$

and

$$\beta_i = 1\Big/\left(\frac{\lambda}{\lambda_1}\,2k'\right)_i \qquad (3)$$

i being 1 or 2. $\lambda$, $\lambda_1$, $\lambda_2$ and $\lambda_3$ are the customary parameters in the Eyring theory of flow[8,16]; k′ is the specific rate of flow when there is no stress; $\beta$ is defined by Equation 3, and is called here the relaxation time since it has the dimensions of time. The subscript, i, signifies that the corresponding quantities belong to the *i* th kind of flow units. The quantity, $x_i$, is the fraction of the area of the shear surface occupied by the *i* th kind of flow units. The wide applicability of Equation 1 has already been shown by many authors.[1,11,31,32,36,37,38,39] As already pointed out by Eyring,[8,16] in the flow process, the bonds connecting the flow unit to old neighbors are broken, and bonds with new neighbors are formed. If the formation of bonds keeps up with bond breaking the original structure of the flow system will be maintained during the flow process, i.e., $x_i$ = constant. However, if this is not the case, a structural change occurs with high shear-rates (i.e., $x_i$ is a function of $\dot{s}$), since flow units flow forward faster than the restoration of the original structure. It is natural to assume that only unit 2, which is non-Newtonian in nature, suffers structural change since the stress acting on it is higher than that acting on Unit 1, the Newtonian unit. Next, the natures of the non-Newtonian and Newtonian units will be considered.

The Newtonian viscosity of high polymers and their concentrated solutions is proportional to $M^{10/3}$, when M, the molecular weight, is larger than a critical molecular weight, $M_c$, whereas $\eta$ is proportional to $M^{4/3}$ when $M < M_c$. In order to explain these phenomena, Bueche[3] and Eyring, Ree and Hirai[10] assumed the presence of entangled molecules. Figure 1 represents schematically a molecule which is entangled with the neighboring molecules, A, B, C, . . . etc. According to the latter authors, the flow of the entangled molecule proceeds by a slalom movement around molecules, A, B, C, etc., and the shear rate of the center of gravity of the molecules is given by the following equation:

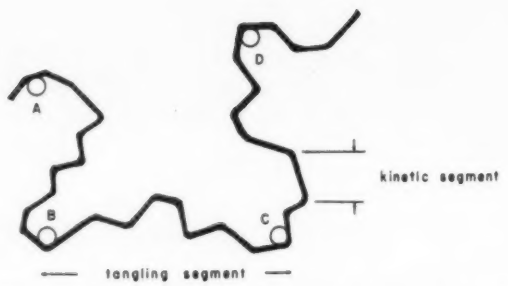


FIGURE 1. Schematic representation of an entangled molecule in a high polymeric system.

$$\dot{s} = \frac{\lambda^0{}'n_1n_2}{\lambda^0{}_1{}'/n_1{}^{1/3}}\;2k'_0n_1\sinh\left(f\lambda^0\lambda^0{}_2\lambda^0{}_3/n_1n_2kT\right) \qquad (4)$$

Here, the superscript and subscript zero, indicates that the attached quantities refer to a kinetic segment of the molecule. $n_1$ is the number of kinetic segments in the molecule, and $n_2$ is the number of tangling segments. The part of a molecule lying between two successive "slalom posts" such as B and C is called a tangling segment. By using the identities, $\lambda = \lambda^0/n_1n_2$, $\lambda_1 = \lambda^0{}_1'/n_1{}^{1/3}$, $k' = n_1k'_0$, and $\lambda_2\lambda_3 = \lambda^0{}_2\lambda^0{}_3$, Equation 4 is transformed to the familiar expression, $\dot{s} = (\lambda/\lambda_1)\,2k'\sinh(\lambda\lambda_2\lambda_3/2kT)$, which when solved for f constitutes the last term in Equation (1). One may readily see that the entangled molecules (non-Newtonian units) form a three-dimensional network.

On the other hand, the physical properties of high polymers, especially the elastic properties, are well explained by the behavior of coiled molecules[13], whose radii are determined by a random distribution of molecular segments.[9,29] The thermodynamics and kinetic properties of high polymeric solutions are also well accounted for as due to randomly coiled molecules.[5,13] Thus, the authors assume that in a flow system there exists two kinds of molecules, the extended entangled ones and the coiled disentangled molecules, the latter being Newtonian. The relative amounts of the respective species are determined by the equilibrium constant for entangled molecule $\rightleftarrows$ disentangled molecule. The equilibrium is noticeably shifted by high stresses. The effect of shear stress on the transition, entanglement $\rightarrow$ disentanglement, is considered below.

### 2. *Flow Equation for a Thixotropic System*

At high stresses, the entangled molecule is stretched as is schematically shown in Figure 2a and disentanglement is promoted (see Figure 2). The free energy barrier for the disentanglement transition is represented by Figure 2b. Here, E and D represent the entangled and disentangled system, respectively. The dotted curve indicates that the barrier for the forward re-

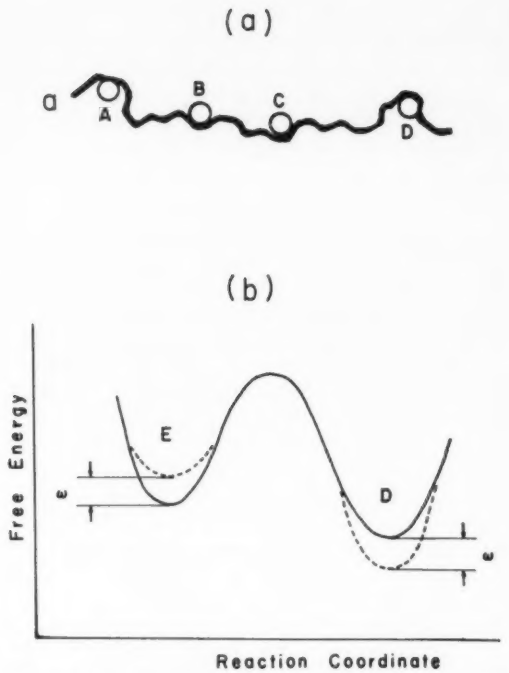


**FIGURE 2. (a) A molecule stretched by a high stress. The strain energy stored in the molecule promotes the transition, entanglement → disentanglement. (b) The free energy barrier for the transition.**

action is lower by an amount of strain energy, $\omega$, while that for the backward reaction is higher by the same amount. The strain energy, $\omega$, is calculated as follows:[22]

$$\omega = \int_0^{s_c} Gsds = G\dot{s}^2/2k_f^2 = c\dot{s}^2 \tag{5}$$

Here, G is the shear modulus of the molecule, $s_c$ is the critical shear at which the transition occurs, where $s_c = \dot{s}/k_f$. The latter relation is obtained from the assumption that the molecular chain elongates during its lifetime as an entangled molecule; here $k_f$ is the specific rate for the forward reaction at $f = 0$.

The net rate of the transition, entanglement → disentanglement, is then given by[16]

$$-\frac{dx_2}{dt} = x_2 k_f e^{\frac{\mu c\dot{s}^2}{kT}} - x_1 k_b e^{\frac{-(1-\mu)c\dot{s}^2}{kT}} \tag{6}$$

For an unsymmetrical barrier, as in the present case, $\mu$ will be different from one half; $k_b$ is the specific rate for the backward reaction at zero stress. When the back reaction is very slow, as actually is the case at high shear rates, Equation 6 is approximated by the equation:

$$-\frac{dx_2}{dt} = x_2 k_f e^{\frac{\mu c\dot{s}^2}{kT}} \tag{7}$$

Experimentally, $\dot{s}$ is changed with time according to the relation:

$$\dot{s} = \rho t \tag{8}$$

Here $\rho$ is a constant which is determined by the experimental conditions. For example, if $\dot{s}$ is raised from zero to $\dot{s}_m$ in time $t_m$, then $\rho = \dot{s}_m/t_m$. Integrating Equation 7 and using Equation 8 yield:

$$x_2 = (x_2)_0 e^{-k_f\gamma I} \tag{9}$$

where $$I = \int_0^y e^{y^2} dy \tag{10}$$

and $$y = \frac{t}{\gamma} = t/\left(\frac{kT}{\mu c\rho^2}\right)^{1/3} = \dot{s}/\left(\frac{kT}{\mu c}\right)^{1/3} = \frac{\dot{s}}{\gamma\dot{f}} \tag{11}$$

$(x_2)_0$ is the fraction of the area occupied by the entangled molecules at $t = 0$. The substitution of Equation 11 into 1 yields

$$f = [1-(x_2)_0 e^{-k_f\gamma I}]\frac{\beta_1}{\alpha_1}\dot{s} + \frac{1}{\alpha_2}(x_2)_0 e^{-k_f\gamma I}\sinh^{-1}\beta_2\dot{s} \tag{12}$$

According to Equation 12, the flow curve, $\dot{s}$ versus f, is time dependent. That is, the curve depends on how fast $\dot{s}$ is raised to $\dot{s}_m$, since Equation 12 includes $\gamma$ which is a function of $\rho$. Here, $\dot{s}_m$ is the fixed maximal shear rate in a series of experiments.

### 3. *Structure of Thixotropic Substances*

As mentioned above, thixotropic substances contain entangled molecules which made a three-dimensional network, and behave as non-Newtonian units. Coiled molecules are contained in the network, and behave as Newtonian units. Thus, the transition, entanglement → disentanglement, which is brought about by stress, destroys the network, changing a solid-like substance to a liquid-like substance.

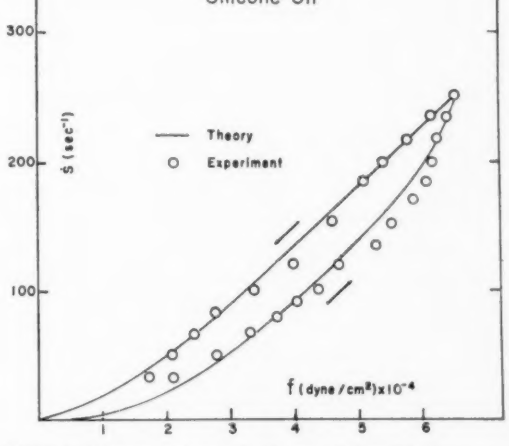


**FIGURE 3. Hysteresis loop of Silicone Oil at 30°C.**

Thixotropy is frequently found in mixtures. For example, grease, which is a typical thixotropic material, is a mixture of soap and lubricating oil. According to recent studies,[2,15,27] the fiber-forming soap molecules develop a three-dimensional network, in which lubricating oil is entrapped. Here, the network-forming "fiber molecules" act as non-Newtonian units, whereas the disentangled fiber molecules and lubricating oil act Newtonianly.

4. *Hysteresis Loop*

A thixotropy curve is composed of two parts: an "upcurve" and a "downcurve" (cf. Figure 3). The upcurve is the flow curve obtained by measuring $\dot{s}$ with increasing f. The flow curve in the reverse direction is the downcurve. As shown in Figure 3, a thixotropy curve has a hysteresis loop. This fact is explained as follows: In the upcurve, entangled molecules transform to disentangled molecules. Only after a prolonged time do the transformed molecules return to the original entangled state. Thus, in the downcurve, the concentrations of entangled and disentangled molecules are constant, and are determined by the concentrations at the apex of the upcurve. Consequently, the downcurve does not coincide with the upcurve. From the above considerations, one easily understands that Equation 12 applies for the upcurve while the following equation applies for the downcurve:

$$f = [1-(x_2)_0\, e^{-k_f\gamma I_m}]\,\frac{\beta_1}{\alpha_1}\dot{s} + \frac{1}{\alpha_2}(x_2)_0\, e^{-k_f\gamma I_m}\sinh\beta_2\dot{s} \tag{13}$$

Here, $I_m$ is the value of I at the apex.

### III. Determination of Parameters

By applying Equation 13 to the downcurve, the parameters, $[1-(x_2)_0\, e^{-k_f\gamma I_m}]\beta_1/\alpha_1$, $[(x_2)_0/\alpha_2]\, e^{-k_f\gamma I_m}$, and $\beta_2$ are determined (cf. references 37 and 38 for the determination of these parameters). The determination of the parameters in Equation 12 involves the following procedures:

1. In the range of very small $\dot{s}$ of an upcurve, Equation 12 is approximated by

$$f = \frac{(x_2)_0}{\alpha_2} e^{-k_f\gamma I}\sinh^{-1}\beta_2\dot{s} \tag{14}$$

Equation 14 is transformed to the following form:

$$\ln\frac{f}{\sinh^{-1}\beta_2\dot{s}} = \ln\frac{(x_2)_0}{\alpha_2} - \frac{k_f}{\rho}\dot{s} \tag{15}$$

Here, Equation 11 and the relation $I \simeq y$ have been introduced, the latter being valid only when $\dot{s}$ is small. Applying 15 to the range of small $\dot{s}$, one obtains the parameters, $(x_2)_0/\alpha_2$ and $k_f/\rho$. Since the parameter, $[(x_2)_0/\alpha_2]\, e^{-k_f\gamma I_m}$, has already been determined, the value of $k_f\gamma I_m$ can now be calculated.

2. Make a graph of I versus y, where the value for I are obtained by a graphical method (cf. Equation 10). Next calculate the quantity, $k_f\gamma I_m/(k_f/\rho)\dot{s}_m$, by using the parameters already determined and the value of $\dot{s}$ at the apex. The above quantity is equal to $I_m/y_m$, because of the following relations:

$$\frac{(k_f\gamma I_m)}{(k_f/\rho)\dot{s}_m} = \frac{I_m}{\dot{s}_m/(\gamma\rho)} = \frac{I_m}{y_m} \tag{16}$$

Here Equation 11 has been introduced. In the graph of I versus y, a straight line is drawn which has a slope of $I_m/y_m$ given by Equation 16 and passes through the origin. The crossing point of the straight line with the curve of I versus y gives $I_m$ and $y_m$. Since one already knows $k_f\gamma I_m$, the parameter, $k_f\gamma$, is calculated. Also, the quantity $\gamma\rho$, is obtained from the relation, $y_m = \dot{s}_m/\gamma\rho$. Generally, $y = \dot{s}/\gamma\rho$. Thus, the value of y corresponding to any $\dot{s}$ is calculated, and the value of I at this y is read from the curve of I versus y.

3. From Equation 12, one obtains

$$\frac{f_a - \dfrac{(x_2)_0}{\alpha_2}\, e^{-k_f\gamma I_a}\sinh^{-1}\beta_2\dot{s}_a}{f_b - \dfrac{(x_2)_0}{\alpha_2}\, e^{-k_f\gamma I_b}\sinh^{-1}\beta_2\dot{s}_b} = \frac{[1-(x_2)_0\, e^{-k_f\gamma I_a}]\dfrac{\beta_1}{\alpha_1}\,\dot{s}_a}{[1-(x_2)_0\, e^{-k_f\gamma I_b}]\dfrac{\beta_1}{\alpha_1}\,\dot{s}_b} \tag{17}$$

In Equation 17, the quantities, $f_a$, $f_b$, $\dot{s}_a$ and $\dot{s}_b$ are the values of f and $\dot{s}$ corresponding to two points, a and b, over the middle range of a flow curve. The quantities, $I_a$ and $I_b$, are the values of I corresponding to $\dot{s}_a$ and $\dot{s}_b$, respectively. Applying Equation 17 to the flow curve, and using the parameters determined above, one can calculate the left term of Equation 17. As a result, the parameters, $(x_2)_0$, $\beta_1/\alpha_1$ and $1/\alpha_2$, are calculated from Equation 17. Thus, all parameters of Equation 12 are determined.

It should be mentioned here that the parameters obtained by the above procedure are adjusted to obtain the best fit of the experimental data. This adjustment is necessary, since the procedure includes rough approximations. For example, in procedure 1, the contribution of disentangled molecules is first neglected, whereas it is about 20 per cent after the adjustment is made. In the above, a flow curve was arbitrarily divided into the ranges of $\dot{s}$'s with small, medium, and large values. Thus, the parameters first obtained over the arbitrary ranges are then adjusted to fit over the entire range.

### IV. Applications

1. *Silicone Oil*

The authors' theory first is applied to the thixotropy curve of silicone oil.[4,7] Silicone has a very low temperature coefficient of viscosity. Thus, the effect of frictional heating during experiments on viscosity are negligible. As a result, the thixotropy curve in Figure 3 is not due to frictional heating, but is due to the structural breakdown of the liquid (cf. the later part). The parametric values obtained by analysing the experimental data are listed in Table I with those obtained for other substances. The full curves in Figure 3 are

calculated from Equations 12 and 13 by using the parametric values. The agreement between theory and experiment is satisfactory.

In the following, the thixotropies of printing ink, shaving cream, mayonnaise, grease and heavy mineral oil will be discussed. Except for heavy mineral oil, the compositions are very complex, and have not been given in the references from which the experimental data were quoted. Thus, the nature of the networks and of flow units are obscure. The authors, however, apply their theory to these substances, since the results are interesting and are important for understanding thixotropy.

2. *Printing Ink*

Green[18] reported a number of thixotropic curves of printing inks and of many other substances. The data were obtained by using a rotational viscometer. Here, the authors analyze only a few interesting cases of the thixotropy curves reported. The original curves in Green's book are expressed in terms of n (the number of revolutions per minute of the outer cylinder of the viscometer) versus the scale reading $\theta$ (the deflection of the inner cylinder). These quantities are transformed to $\dot{s}$ and f, respectively, by the following equations:[10]

$$\dot{s} = \frac{4\pi n}{60[1-(R_b/R_c)^2]} \qquad (18)$$

$$f = \frac{K\theta}{2\pi h R_b^2} \qquad (19)$$

Here, $R_b$ and $R_c$ are the radii of the bob and of the cup of the viscometer, respectively. K is the torsional constant; h is the height of the liquid. These instrumental constants are given by Green.[18]

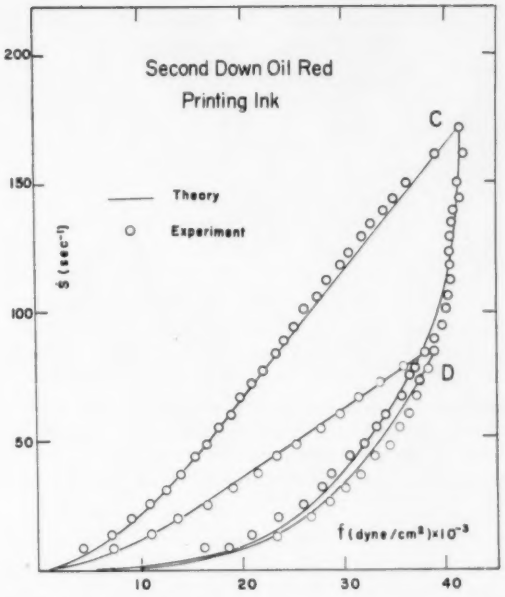


**FIGURE 4. Hysteresis loops of "Second Down Red Printing Ink" at 30°C. Curve C represents a large loop while D indicates a small one.**

The experimental points in Figure 4 were obtained from Green's data[18] for a "second-down oil red printing ink." Figure 4 contains two hysteresis loops, C and D. The experimental conditions for the two loops are the same except that D has a lower $\dot{s}_m$ than does C. Thus the discrepancy in the upcurves of C and D is considered to be a systematic experimental error. The theoretical curves were calculated from equations 12, and 13 by using the parametric values in Table I.

**TABLE I*—Parametric Values for Hysteresis Loops**

| | | $\gamma\rho$ | $k_f\gamma$ | $(x_2)_0$ | $(x_2)_m$ | $\beta_1/\alpha_1$ | $\beta_2$ | $1/\alpha_2 \times 10^{-4}$ | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| Silicone Oil | | 153 | 0.089 | 0.10 | 0.060 | 215 | 0.50 | 4.78 | 44 |
| [Second Down Oil] | l | 114 | 0.347 | 0.10 | 0.025 | 200 | 6.00 | 4.28 | 18 |
| [Red Printing Ink ] | s | 114 | 0.121 | 0.10 | 0.034 | 359 | 6.00 | 4.28 | 18 |
| Shaving Cream | | 138 | 0.300 | 0.10 | 0.053 | 2.00 | 1.38 | 0.101 | 18 |
| Heavy Mineral Oil | | 239 | 0.100 | 0.20 | 0.147 | 212 | 0.012 | 27.5 | 42 |
| Red Printing Ink | l | 125 | 0.282 | 0.10 | 0.028 | 119 | 1.66 | 1.44 | 18 |
| | s | 125 | 0.513 | 0.10 | 0.066 | 133 | 1.66 | 1.44 | 18 |
| [Light Chrome ] | l | 150 | 0.400 | 0.20 | 0.083 | 169 | 1.00 | 1.73 | 18 |
| [Yellow Printing Ink] | s | 150 | 0.948 | 0.20 | 0.110 | 217 | 1.00 | 1.73 | 18 |
| Mayonnaise | | 187 | 0.100 | 0.20 | 0.177 | 5.00 | 1.15 | 0.118 | 18 |
| Grease S | | 759 | 0.137 | 0.10 | 0.026 | 23 | 3.00 | 2.35 | 45 |
| | | 759 | 2.57 | 0.10 | 0.034 | 51 | 3.00 | 2.35 | 45 |

* The letters, l and s for Second Down Oil Printing Ink, Red Printing Ink, and Light Chrome Yellow Printing Ink indicate that the parametric values were obtained from the large and small loops of the thixotropic curves, respectively. The upper and lower parametric values for Grease S were obtained from Figure 3 and 4 of Reference 45 respectively.

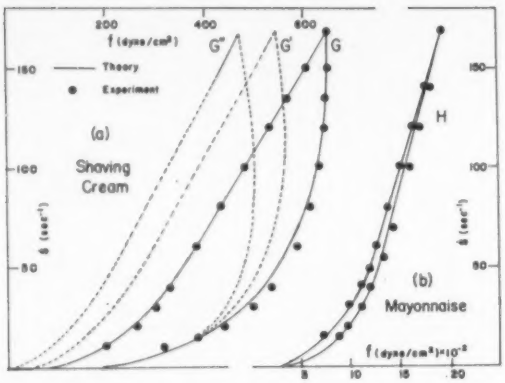


FIGURE 5. (a) Hysteresis loop of shaving cream at 30°C. Curves G, G′ and G″ were calculated from Equations 12 and 13 by using the same parameters except for $\rho$ which decreased in the proportions, 1: 0.61 : 0.43. (b) Thixotropy loop of mayonnaise at 30°C.

### 3. *Shaving Cream and Mayonnaise*

These substances are very familiar in daily life. As shown in Figure 5, both are thixotropic. The theoretical curves, calculated from Equations 12 and 13, are shown in Figure 5.

In Table I, the results obtained for the substances, whose thixotropy curves are not shown here, are also tabulated.

## V. Discussion

### 1. *Stress Relaxation*

If a thixotropic system is sheared at a constant rate of shear, the stress decreases with time, approaching an equilibrium stress, $f_E$, with sufficiently long elapsed time. This is due to the breakdown of structure. In this case, the second term on the right of Equation 6 is not neglected. Thus, $x_2$ is given by the following equation:

$$x_2 = [(x_2)_0 - \frac{b}{a}]e^{-at} + \frac{b}{a} \tag{20}$$

where,
$$a = k_f e^{\frac{\mu c\dot{s}^2}{kt}} + k_b e^{\frac{-(1-\mu)c\dot{s}^2}{kT}} \tag{21}$$

and
$$b = k_b e^{-\frac{(1-\mu)c\dot{s}^2}{kT}} \tag{22}$$

By substituting Equation 20 into 1, one obtains

$$\ln(f - f_E) = p - at \tag{23}$$

where
$$f_E = \frac{b}{a}\left\{\frac{\sinh^{-1}\beta_2\dot{s}}{\alpha_2} - \frac{\beta_1}{\alpha_1}\dot{s}\right\} + \frac{\beta_1}{\alpha_1}\dot{s} \tag{24}$$

and
$$p = \ln\left[\left\{\frac{\sinh^{-1}\beta_2\dot{s}}{\alpha_2} - \frac{\beta_1}{\alpha_1}\right\}\left\{(x_2)_0 - \frac{b}{a}\right\}\right] \tag{25}$$

Weltmann[42] measured the decrease of stress when mineral oil was sheared at various constant rates. Using the same sample, she also obtained a hysteresis loop,

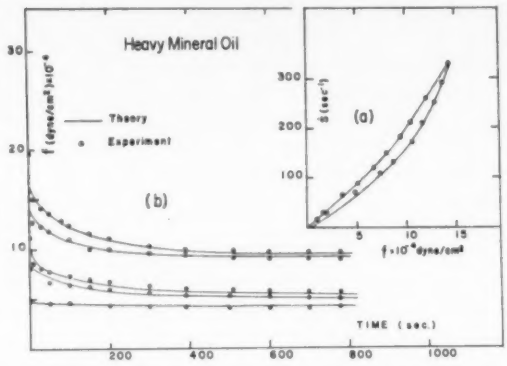


FIGURE 6. (a) Hysteresis loop of Heavy Mineral Oil at 30°C. (b) Relaxation of stress in Heavy Mineral Oil at 30°C. The theoretical curves were calculated from Equation 23 by using the parameters obtained from the analysis of the hysteresis loop in Figure 6a.

as shown in Figure 6a. The parameters occurring in Equations 20-25 are determined from the hysteresis loop. Thus, from the hysteresis loop, one can predict the stress-relaxation experiments. The values of $\beta_2$, $k_f$, $\gamma\rho$, $(x_2)_0$, $1/\alpha_2$ and $\beta_1/\alpha_1$, which are determined from the loop (cf. Figure 6a), are tabulated in Table I. By using these values, the quantities, a, c/kT, $f_E$, and p are

TABLE II*

Stress Relaxation of Heavy Mineral Oil

| $\dot{s}$ | $\frac{c}{kT} \times 10^5$ | $f_E$ $\frac{dyne}{cm^2} \times 10^{-4}$ | p | $a \times 10^3$ |
|---|---|---|---|---|
| 330 | 1.45 | 9.45 | 11.2 | 7.76 |
| 254 | 1.45 | 9.39 | 10.8 | 5.88 |
| 168 | 6.63 | 5.16 | 10.9 | 8.21 |
| 117 | 6.63 | 5.03 | 10.4 | 5.92 |
| 61 | 6.63 | 4.12 | 8.8 | 4.53 |

* The values of $\dot{s}$ in the first column indicate the rates of shear under which the relaxation experiments were conducted.

calculated, and summarized in Table II. Here the values of $\rho$ and $\mu$ have been taken as 8.0[44, 45] and ½, respectively. The relations, $k_f/k_b = (x_2)_0/[1-(x_2)_0]$ and $1/\gamma\rho = (\mu c/kT)^{1/2}$, have also been introduced. The theoretical relaxation curves are calculated from Equation 23 by using the parameters listed in Table II,* and are shown in Figure 6b. The predicted curves agree very well with the experimental curves. This agreement indicates that the authors' theory is correct. It should be mentioned here that Weltmann[43] claims the following relation for her data in stress-relaxation experiments: $f = -a'\ln t + b'$, where a′ and b′ are con-

* The values of c/kT for the first two experiments differ from those for the last three experiments. This difference may be due to some differences in the experimental conditions. By examination, one actually finds that the last three relaxation curves[42], are located farther below the first two than one would expect theoretically.

stant. According to the authors' test, however, the plots of f versus ln t are sigmoidal almost in all cases, while Equation 23 holds exactly.

2. *Time Effect*

In Figure 5, the dotted curves, G′ and G″, are calculated from Equations 12 and 13 using the same parameters as for curve G, except for the parameter, $k_f\gamma$. That is, for the calculations of G′ and G″, the values, 0.5 and 0.7, were used for $k_f\gamma$ instead of 0.3 which was used for curve G. According to Equation 11, $\gamma$ is inversely proportional to $\rho$. Thus, the values of $\rho$ decreased in the ratios, 1 : 0.60 : 0.43, for calculating curves, G, G′ and G″, respectively. From these curves one sees that if more time elapsed during the raising of the rate of shear to a fixed maximal value, $\dot{s}_m$, the flow curve turns toward the $\dot{s}$ axis in the plot of $\dot{s}$ versus f, as shown in Figure 5. Green[18] claims in his book that this fact was observed experimentally, and he represents the experimental facts by curves which are exactly similar to our curves G, G′ and G″.*

3. *Frictional Heating*

Weltmann[44] as well as Lower, Walker and Zettlemoyer[30] found that in the experiments with a rotational viscometer the temperature of samples rose because of the heat evolved by friction. There are a number of disputes concerning the softening of samples with shear. One school[21,24,25,30,33] contends that the softening is due to the temperature increment by friction, while the other[1,7,17,18,19,20,26,28,34,42,43,44] ascribes it to structural breakdown with shear. The authors believe that the data treated here are due to the latter. The reasons are as follows: (1) Most of the samples are semi-solid at rest, while they change to liquid with high shear rates. (2) Weltmann[44] confirmed experimentally that the hysteresis loop does not change appreciably with the frictional temperature rise. (3) The theoretical calculations by Weltmann and Kuhns[46] and by Johns and Tyson[28] also provide good reason for believing that the above result obtained by Weltmann[44] is true and that the hysteresis loop is mainly due to structural change. (4) In the experiments of Green and Weltmann, hysteresis loops over a wide range of shear were obtained within one minute. Consequently the heating effect was minimized. Thus, the authors treated the experimental data, which were analysed in this paper, as due to structural breakdown. Of course, some correction of the data for the frictional heating may be necessary. In a second approximation, however, the correction is neglected because of the reasons mentioned above, and because of lack of necessary data for making the correction.

4. *Newtonian Viscosity*

In the above, it has been assumed that the non-Newtonian units have a uniform structure, i.e., that every non-Newtonian molecule has the same degree of entanglement. It is, however, more probable that among the non-Newtonian type molecules there exist various types which differ in the degree of entanglement. Similarly, the Newtonian units include various types of molecules which differ in the degree of disentanglement. In view of these facts, the parameters, $\beta_1/\alpha_1$, $\beta_2$, etc., in the author's theory should be considered as the average values of the corresponding quantities. The average values may change with experimental conditions.

The data summarized in Table I indicate that the Newtonian viscosity, $\beta_1/\alpha_1$, which was obtained from a large loop of thixotropy curves, is smaller than the corresponding quantity obtained from a small loop. As already mentioned, the large loop has a larger value of $\dot{s}_m$ than does the small loop, i.e., the material has on the average been destroyed under a higher shear rate over a longer period. Thus, the downcurve for the large loop contains Newtonian molecules whose average value of $\beta_1/\alpha_1$, is smaller than in the small loop.*

Similarly, the average value of $\beta_2$ for a large loop is smaller than that for a small loop. But, $\beta_2$ is an insensitive quantity for fitting data, since it occurs in the argument of an hyperbolic arcsine function. Thus, $\beta_2$ has been assumed to be constant for both the large and small loop.


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* It is regrettable that the authors cannot find experimental data for the curves G′ and G″, since neither Green[18] nor Weltmann[44,45] represent the data for "the time effect" in the fashion which the authors require, but only schematically.

* When a thixotropic system contains solvent molecules, the viscosity of the solvent does not change with shear rate. Thus, the above discussion refers only to the Newtonian units formed from non-Newtonian units.

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# The Analysis of Fatty Acid Esters by Gas Chromatography

By: Nathaniel Brenner
Phillip Scholly
Lawrence O'Brien

The Perkin-Elmer Corporation

GAS CHROMATOGRAPHY PROVIDES a powerful means for the separation of complex mixtures of volatile materials into individual components. This separating power may be used for preparation of pure materials, or, much more generally, for the qualitative and quantitative analysis of the samples.

The Vapor fractometer is shown schematically in Figure 1. A very small sample (1-10 mg.) of the sample mixture is injected into the unit and is vaporized by a heater in the liquid injection block. It is mixed with the inert carrier gas which flows constantly through the system. The carrier gas–sample mixture then enters the tubular column which is packed with

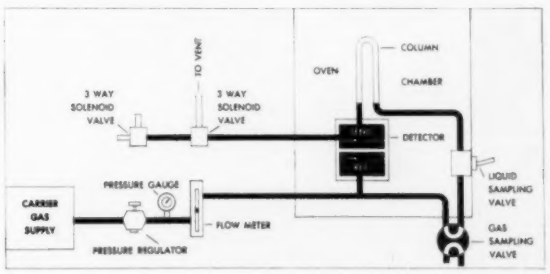


FIGURE 1, flow schematic of model 154-C vapor fractometer

a fine granular material, such as diatomaceous earth, upon which has been coated a thin layer of a selected non-volatile oil. As the mixture passes through the column, the various components in the sample will travel at different rates which will be inversely proportional to their solubilities in the oil substrate. The material which by reason of extreme volatility or insolubility has the least affinity for the column substrate will pass completely through the column first and the other components will arrive at the far end of the column in order of increasing affinity. At the end of the column, the "eluted" components pass in order through a detection cell, generally of a type which electrically measures some physical property of the sample component which differs markedly from that of the carrier gas. By comparing the resultant electrical signal with that obtained by an identical "reference" cell which contains only carrier gas, we can obtain a differential measurement which is proportional to the amount of sample component being eluted from the column at any time. The physical property measured by detectors in most general use today is that of thermal conductivity. The electrical signal derived is amplified and recorded on a standard strip chart potentiometer recorder.

The exterior of the complete Vapor Fractometer is shown in Figure 2. The oven in which the column and detector are contained may be heated to any temperature up to 2250°C if necessary, and its temperature held constant by a thermostat controller. The samples which are treated in this work are composed of methyl esters of fatty acids ranging in carbon number from 4 to 20 with most emphasis on the $C_{16}$ to $C_{20}$ group. A temperature of 210° C was found to be most satisfactory for the rapid analysis of these materials. Figure 3 illustrates the analysis of a mixture of saturated and unsaturated esters of the $C_8$ to $C_{18}$ acids. The position of each peak in the chromatogram is characteristic of the specific compound. Therefore, the "elution time" shown at the bottom of the illustration serves to identify the components qualitatively. Since the electrical difference signal from the detector is at any moment proportional to the quantity of component in the detector, the total area under a peak is proportional to the total amount of that component present in the sample. For example, by simple visual inspection of Figure 3, we can see that the sample contains large amounts of stearate and linoleate, considerable quantities of oleate and palmitate, smaller amounts of linolenate, myristate, laurate, caprate, caproate, and palmitoleate and traces of esters lower in carbon number than caproate.

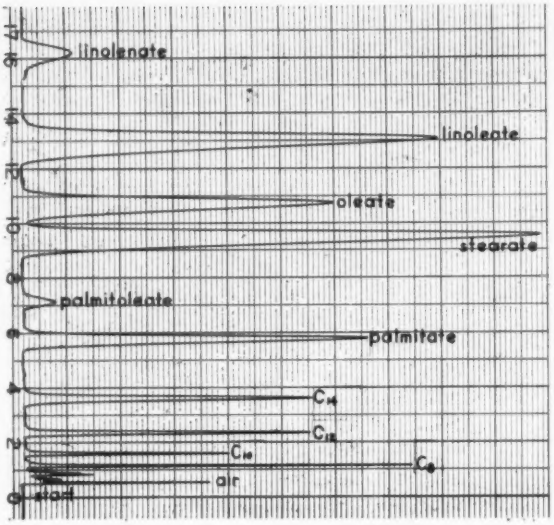


FIGURE 3, this is the result—a complete qualitiative analysis in 17 minutes

To obtain an accurate percentage composition of the various components, measurement of the area under each peak would be made. This could be done by planimetry, triangle area calculation, or the use of electrical or mechanical integrating devices. When all

FIGURE 2, technician setting vapor fractometer controls for an analysis of a mixture of fatty acid methyl esters.

FIGURE 4, accurate quantitative analyses may be made with this Perkin-Elmer model 194 printing integrator.

areas have been measured, the total of these figures represents 100% of the sample. The ratio of the area of each peak to the total area now represents the concentration of that component. The calculation is, therefore:

$$\text{Component concentration} = \frac{\text{area under component peak} \times 100}{\text{total area under all peaks}}$$

In this work, calculation of individual and total peak areas was performed automatically by a Perkin-Elmer Printing Integrator. This device, shown in Figure 4, attaches to standard potentiometer recorders and automatically computes the area included under each peak as it is recorded by changing the velocity of a counting device proportional to the displacement of the recorder from the base line. At full scale the counter will run at a rate of 6000 counts per minute. This high count rate, plus a linearity of better than 1 per cent make possible a very accurate area determination. The integrator will print the counter figure at the beginning of each peak as shown in Figure 5. The area is therefore equal to the difference between the counts printed at the beginning of a peak and that shown at the beginning of the succeeding peak. The final printed figure is obtained by manually actuating the integrator. (This is necessary since the device records at the start of a peak. In order to obtain the figure for the final peak we must print the figure at the end of the last peak since there are no subsequent peaks). The total area under all peaks is the difference between this last figure and the first printed figure in the run. Example: In Figure 5.

$$\text{Area of peak A} = (23619) - (22282) = (1337)$$
$$\text{Total area} = (26561) - (22282) = (4279)$$
$$\text{Concentration of component A} = \frac{(1337)}{(4279)} \times 100 = 31.1\% \text{ of sample}$$

As shown in the illustration, the speed of the integrator recording tape may be synchronized with that of the strip chart recorder. This permits the quick assignment of numbers to their corresponding peaks since the integrator tape can be laid directly alongside the chromatogram and a visual correlation made.

Fats are analyzed in the form of methyl esters rather than as glycerides, soaps or free acids because of the higher volatility of the esters. The free acids were analyzed by James & Martin[1] in the first work in gas chromatography and indeed acids up to palmitic are readily separated, but recent work has been primarily devoted to obtaining higher efficiencies in separation of the esterified materials.

Probably the most important contributions to the development of an efficient chromatographic method were those made in the development of columns of

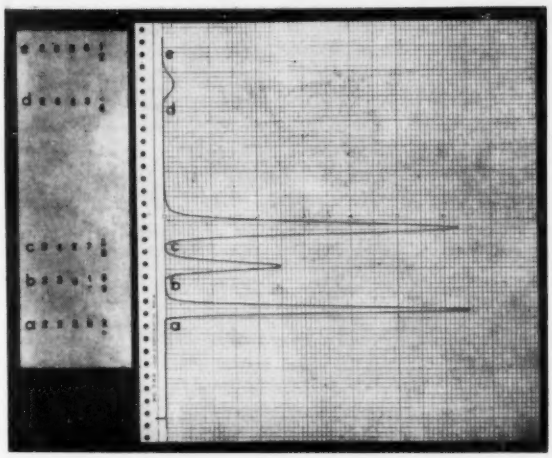


**FIGURE 5, integrator tape giving quantitative values matches easily with peaks on chromatogram.**

high separating power. Drs. Callen and Orr[2] of Procter and Gamble introduced the use of polyester resins as column substrates. These materials were the first to separate the $C_{18}$ unsaturated esters completely from each other and from the stearate ester. Further work on polyesters by Dr. Lipsky[3] at Yale university and by Dr. Tove at North Carolina State university developed particularly effective columns using the polyesters of succinic acid. A succinic acid polyester of particularly high stability is the material of which the column used in this work has been fabricated.

The edible oils used in the comparative part of this study were obtained from Mr. Roy W. Riemenschneider of the U.S. Department of Agriculture's eastern regional research laboratory. The esterification

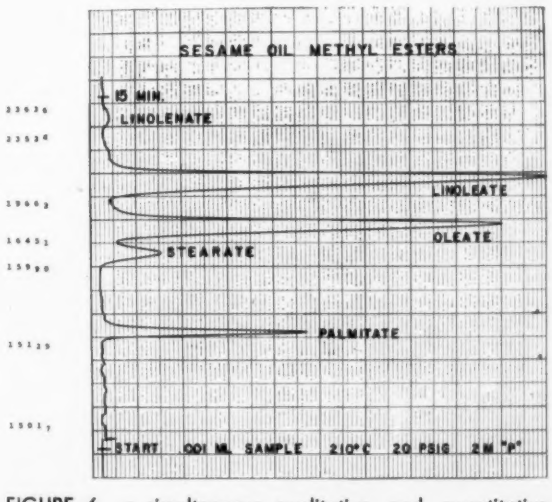


**FIGURE 6, a simultaneous qualitative and quantitative analysis of sesame oil methyl esters in less than 20 minutes.**

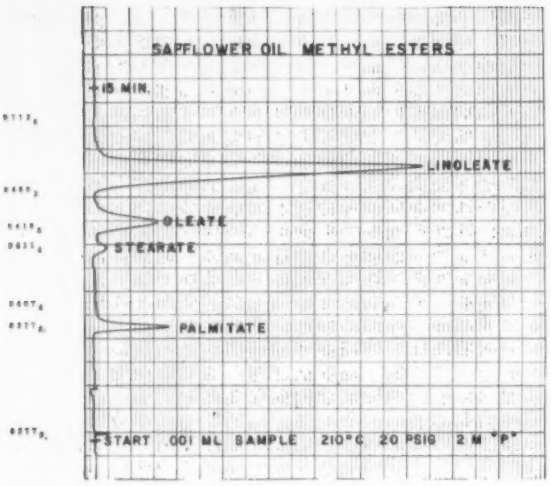


FIGURE 7, analysis of safflower oil

procedure and iodine value determinations were also performed by his group.

Figure 6 shows a run of sesame oil esters. It should be noted here that each chromatogram shown has been run at a single "sensitivity" level. That is, all peaks of equal height represent equal detector signal level. That is contrary to general practice, where large component peak signals are "attenuated," (divided) to stay within the recorder chart limits while trace components are run at full sensivity. The method shown here preserves the visual integrity of the samples since all peaks are graphically proportional to component concentration.

The concentrations of the components as obtained from the integrator figures alongside, is shown alongside each component.

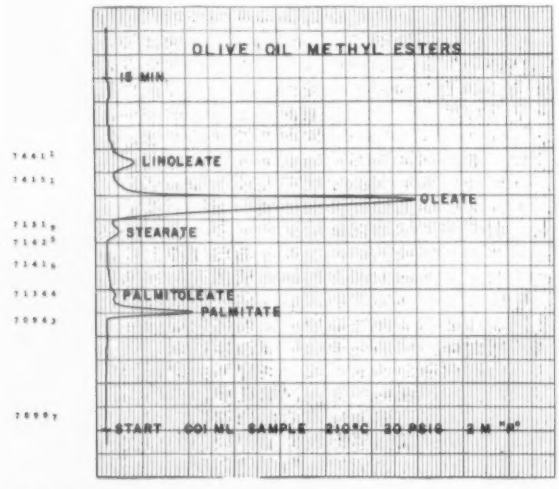


FIGURE 8, analysis of olive oil

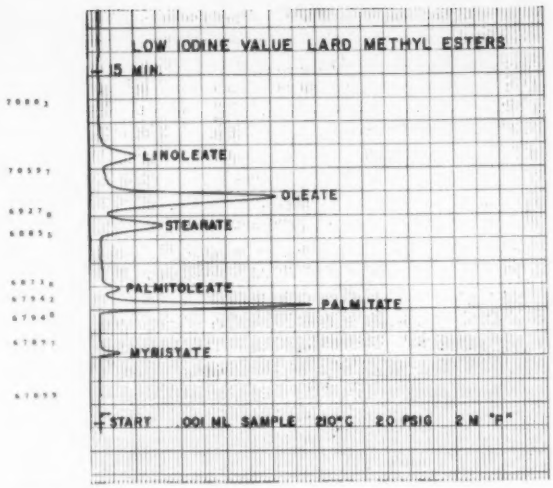


FIGURE 9, an analysis of low iodine value lard methyl esters. This pig was put on a standard diet relatively low in linoleic acid.

Figure 7 shows the results of the same procedure with a sample of safflower oil.

Figure 8 is a result of the analysis of olive oil.

Figures 9 and 10 show two chromatograms of two lard samples one of iodine value 59 and the other 120. The chromatograms clearly show the higher level of linoleate responsible for the higher I.V. of the second sample. The striking distinction in these samples is attributed to the diet differences between the hogs from which the lard originated.

The Table presents the complete results of the analyses. The results obtained with the Vapor fractometer (V.F.) are averages of two or more analyses of each sample. The columns marked U.V. are re-

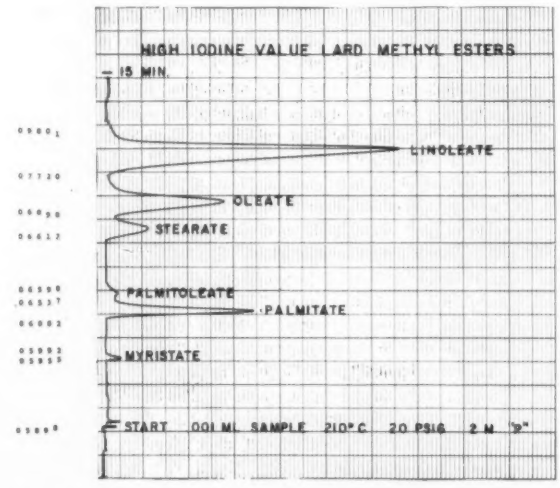


FIGURE 10, an analysis of high iodine value lard methyl esters. This pig was put on a diet rich in linoleic acid.

**% COMPOSITION OF METHYL ESTERS OF EDIBLE OILS**

| *Method* | $C_{14}$ | $C_{16}$ | $C_{18}$ | *Palmit-oleate* | *Oleate* | *Lin-oleate* | *Lin-olenate* |
|---|---|---|---|---|---|---|---|
| LARD—LOW IODINE VALUE—59.1 | | | | | | | |
| Fractometer | 1.5 | 26.9 | 14.1 | 4.3 | 43.8 | 9.5 | ... |
| | | Total 42.5 | | Total 48.1 | | | |
| Ultraviolet | | Total 42.7 | | Total 47.0 | | 8.9 | 0.6 |
| LARD—HIGH IODINE VALUE 119.9 | | | | | | | |
| Fractometer | 1.0 | 14.0 | 7.3 | 1.4 | 21.8 | 54.6 | ... |
| | | Total 22.3 | | Total 23.2 | | | |
| Ultraviolet | | Total 21.0 | | Total 21.1 | | 56.3 | 1.0 |
| SESAME—IODINE VALUE 112.7 | | | | | | | |
| Fractometer | | 11.6 | 5.3 | ... | 37.6 | 44.0 | 1.5 |
| | | Total 16.9 | | | | | |
| Ultraviolet | | Total 13.3 | | Total 43.2 | | 42.7 | 0.8 |
| SAFFLOWER—IODINE VALUE 144.2 | | | | | | | |
| Fractometer | | 7.5 | 2.1 | ... | 13.8 | 76.6 | ... |
| | | Total 9.6 | | | | | |
| Ultraviolet | | Total 8.8 | | Total 15.0 | | 76.2 | ... |
| OLIVE—IODINE VALUE 81.8 | | | | | | | |
| Fractometer | .. | 11.7 | 2.2 | 1.4 | 77.1 | 7.5 | trace |
| | | Total 13.9 | | Total 78.5 | | | |
| Ultraviolet | | Total 11.8 | | Total 81.6 | | 5.9 | 0.7 |

sults obtained by analysis for polyunsaturation by alkali isomerization and ultraviolet spectrophotometry[4], calculation of monounsaturation (as oleate) from the iodine value—polyunsaturate difference, and finally saturates by difference from 100 per cent. It should be noted that the spectrophotometric method determined trace tetraene and pentaene where the fractometer did not. However, the former method errs by including all monounsaturates as "oleate" and by failing to determine the exact nature of saturated esters as well. Therefore, while neither method gives absolute accuracy, it may be generalized that the results using the gas chromatograph and U.V. + iodine number system are in good agreement. The U.V. method is more sensitive to trace polyunsaturation, the gas chromatograph is better able to qualitatively assign concentrations to individual saturated or monounsaturated components.

Figures 11 and 12 show the application of the meth-

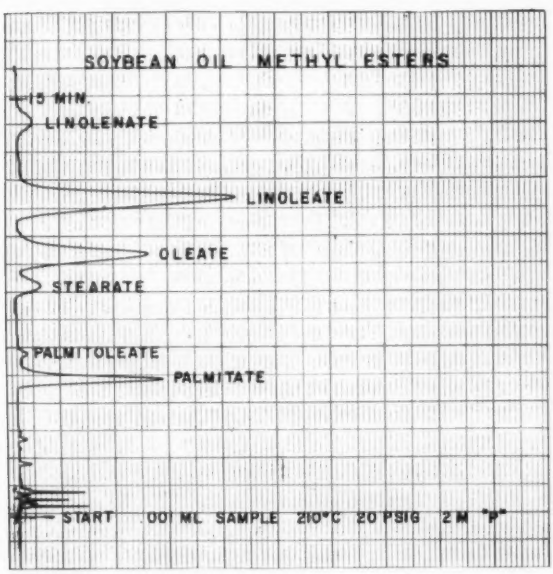


FIGURE 11, analysis of soybean oil

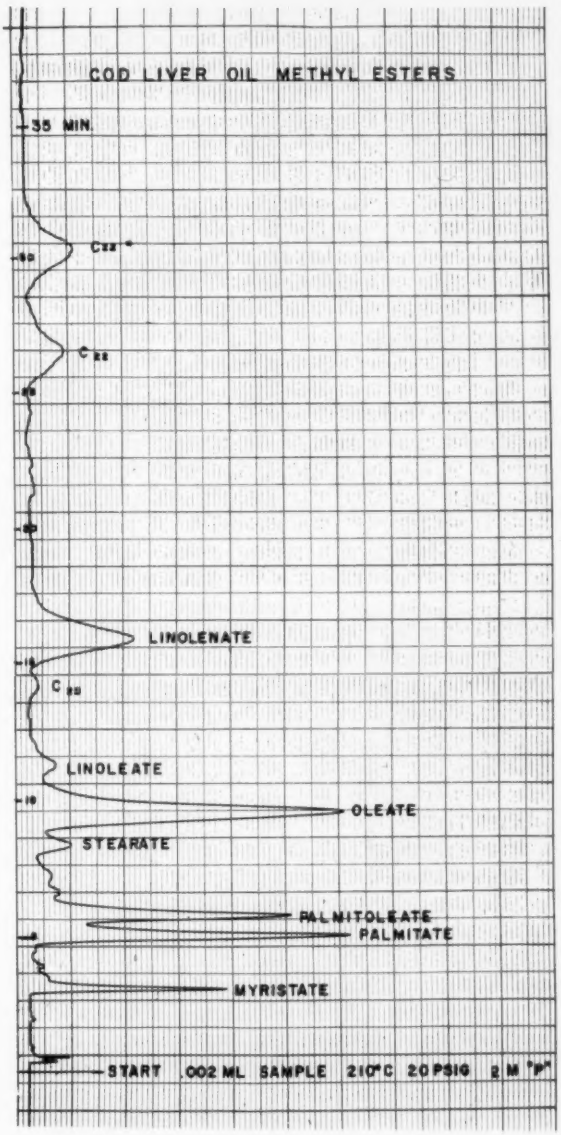


FIGURE 12, analysis of cod liver oil

od to two oils not included in the comparative study; soybean and cod liver oil.

They are included merely to show that the method is applicable to other oils, even those as distinctive in composition from seed oils as cod liver oil.

The time required for production of each of the oilseed ester chromatograms was about 20 minutes. If a printing integrator is used about 5 minutes of calculation time is required to complete the analysis. While the conversion of the oils to methyl esters is admittedly a time consuming procedure, it is certainly less difficult and requires less careful manipulation than does the alkali isomerization technique.

Given the methyl esters as a working sample, the Vapor fractometer can yield a fast analysis of the material with the following advantages:

1. No manipulation required during the analysis except for sample injection.
2. A permanent record of the sample showing a graphic representation of concentration of each component.
3. Complete separation of all components of interest, whether their presence is previously suspected or not.
4. Non-destructive separation of components, permitting collection of any "unknown" component for subsequent analysis by ancillary methods.

The results described above have been submitted to Mr. R. W. Riemenschneider of eastern regional research laboratory, U.S.D.A., Wyndmoor, Pennsylvania for inclusion in his general investigation of analytical methods for fatty acid composition. Results of this larger program will be published shortly.

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4. Herb, S. and Riemenschneider, R. W., A Spectrophotometric micromethod for Determination of Polyunsaturated Fatty Acids. *Anal. Chem.* 25 (June, 1953), P. 953.


## About the Authors

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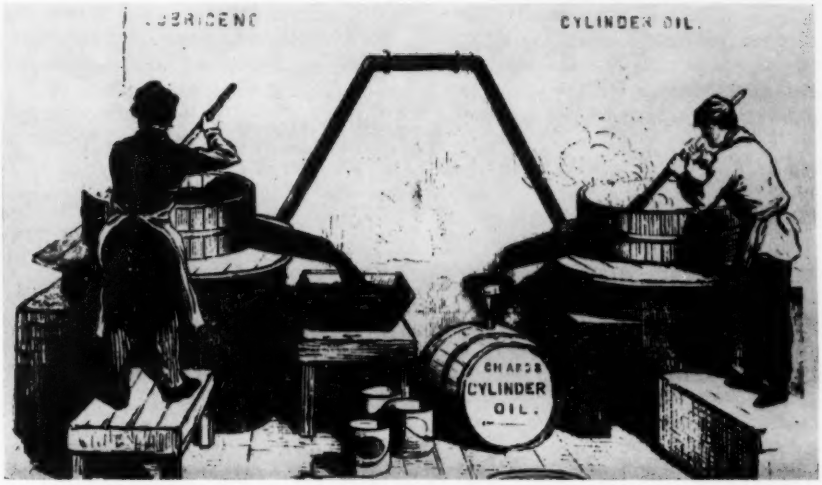
1859




1959

# OIL'S FIRST CENTURY

## Hobbled by Inadequate Lubricants, America's Industrial Revolution Put Mechanical Energy to Work After Petroleum Progress Was Introduced

We celebrate this year the 100th anniversary of the Drake well because the method of bringing in this well represented an 1859 technological breakthrough—not to suggest that oil is only a century old.

Many references are found in ancient books to oil. The Greeks had a word for it and it is believed that a number of the substances mentioned in the Bible contained oil. But this, of course, was before man went underground to find oil. In primitive times rock oil or "petroleum" to give the Greek coinage—oozed from mineral outcroppings or was noted as a film on water. The inhabitants of areas where this occurred found that the dark liquid had certain practical uses and often regarded it as medicinal in nature.

So our ancestors of remote ages employed it for waterproofing, for bodily adornment and, when so inclined, for purposes of therapy. Medieval scientists labeled it as "petroleum" and by the time America was discovered people in many parts of the world were aware that oil had some sort of usefulness and that it was one of the blessings conferred by the good earth.

*Not so where lubrication was concerned, however. One early nineteenth century recipe . . . for the lubrication of church bells, went something like this: "The gudgeons of church bells get dry and increase friction and thus labour the ringers. To keep bearings sweet and free, take four pounds of the honey of the honey bee and boil it up. To this add one pint of sheep's blood and bring to the boil. Melt two pounds of hog's lard in another pot and when thin, add this to the honey pot and well mix and remix until all is in full compound liquid. Pour into a flat pan and cool. This grease should be applied to the bell gudgeon and the bell swung until it works into the bearing."*

The Spanish Conquistadores found evidence among the Indians of the presence of oil in the New World. The aborigines used it for medicine as well as an ingredient for war paint. The Spaniards utilized boiled-down oil found on the beaches for a more practical

purpose—that of caulking leaks in their vessels. Early settlers of this country followed native example in using surface oil for crude lubrication; and they, too, regarded it as medicinal. "Seneca Oil"—a refinement of the crude—found its way into many an early American medicine cabinet.

In the early eighteen fifties American ingenuity had started to think in terms of a larger use of this natural resource. The early search, of course, had little immediate relation to the uses of oil such as were current in 1859. What the America of that period seemed to need most desperately was a practical lamp oil to improve the illumination of its growing cities. Whale oil and coal oil were the staples of the time for this purpose—and both were expensive, smelly and smoky. Also, the 50 "coal oil" plants of the country produced only 22,750 gallons annually. A Colonel A. C. Ferris of New York put down a shaft at Tarentum, Pa., in 1857 with the hope of bringing in petroleum in quantity—but failed to hit. Then the Drake well proved the practicality of drilling.

The Drake well ushered in an era of ample fuel energy into a world hedged in then by limitations on both light and power. Henceforth, sperm oil and coal oil were to be outmoded by petroleum, the marvelous earth fluid which was to power the many inventions of the forth coming industrial revolution. The age of oil triggered developments which were to lead into the hectic period wherein would be invented the auto, the airplane, etc.

*Where lubricating grease was concerned, until close to* 1800 *the universal lubricant was beef or mutton tallow, or a vegetable oil. After the Drake well the first lubricating grease as we know it today began being manufactured. But lubrication presented no problems at that time . . . as the Industrial Revolution progressed, the picture changed, and proper lubrication became of extreme importance to industrial progress.*

Colonel Drake's well, striking oil at 69½ feet, was put down at the rate of three feet per day. The derrick and equipment combined weighed a mere ten tons and well-bottom pressure encountered was negligible—amounting to only an estimated ten pounds per square inch. The completed well produced 15 to 20 barrels daily and the output was sold at the beginning for $18 to $20 per barrel. Whale oil, which had risen to $100 per barrel, had a competitor. However, even this first producer had trouble, the price of Drake's oil dropping to $10 a barrel in 1860 and plummeting to ten cents a barrel by the end of 1861.

During the following two decades oil exploration swiftly cast off its toddling clothes. Basic geological principles formulated between 1875 and 1885 by John F. Carll of the Pennsylvania second geological survey spurred the hunt. He established the fact that oil wasn't in underground caverns or fissures, as first assumed, but existed in the pores of limestone. He further proved that natural gas was in solution in the fluid and could be effective in bringing oil to the surface.

Supplementing these findings were the conclusions of geophysicists who employed scientific instruments to show that certain earth structures were likely gas and oil deposits. Scientists from Europe introduced gravity work in this country late in 1922 and thereafter the use of torsion balances became increasingly significant in successful oil exploration.

Paralleling this progress in finding oil was the development of facilities to bring it to the surface, refine it and transport it. William Barnsdall and William H. Abbott built a refinery near Titusville, Pa., in 1860 and placed it "on stream" in January, 1861. From here the refinery was to accompany oil on its march around the world. In 1865 the first successful pipeline was laid in Pennsylvania. By 1870 lubrication oils were being developed. In 1869 the first sea-going vessel fitted with iron tanks for transporting oil was put in service and by 1881 pipelines crossed the Allegheny mountains to the Atlantic seaboard.

*Hiram B. Everest, a Rochester, N. Y., grocer, became a pioneer marketer of petroleum lubricants. In* 1866 *he discovered that after kerosene had been removed from petroleum by distillation, under vacuum, the residue was unscorched. He decided to sell this residue as a lubricant in place of the animal and vegetable fats being used. Everest invested all his money in a shed-sized oil plant, only to be met with scorn by investors and users of lubricants. Down to his last dollar, he packaged his product in salvaged oyster cans and peddled it from shop to shop in a hand cart. Machinists and harness makers one by one agreed to sample Everest's product. One by one they were convinced.*

Acceptance of these new natural resources spread phenomenally, with oil consumption increasing to 150 million barrels by 1900. In this same year petroleum and natural gas provided one-twelfth of this nation's power requirements. This ratio was to increase to one-third by 1930 and to two-thirds in the present year. The early 1900s was the period of the development of gasoline and diesel fuel.

*During the Twenties the stiff competition for the motorist's dollar got many marketers to give service and sell other products. In lubrication, they began adding lube bays to stations, and pits or lifts for getting under the car.*

Their use was multiplied by the urgencies of two world wars and by the expanding transportation facilities of the country. In 1917 world consumption of oil stood at about 500 million barrels. This year it is expected to approach seven billion barrels, the vast expansion of the petrochemical industries providing the setting for the development of a myriad of new products produced from oil. ■

# United Co-Operatives Inc. Joins NLGI

COMPLETED in October, 1957, this one-half million dollar office building in Alliance, Ohio, is the main office of the vast farm supply organization known as United Co-Operatives, Inc.

United Co-Operatives, Inc., with headquarters in Alliance, Ohio, is an organization engaged in the manufacture and procurement of farm supply products. It is vitally concerned about the welfare of farm people everywhere. To this end, it aims to provide quality farm supply products which will last longer and give the farmer better service, at no increase in cost.

Quality, however, is the standard which guides United. Price, while of importance, is by policy a secondary consideration.

### A Co-Operative Is Born

Three regional farm cooperatives—Indiana Farm Bureau Cooperative, Ohio Farm Bureau Service Company and Farm Bureau services of Michigan—in 1930 joined together and formed the Farm Bureau Oil company. Prime purpose of this new organization was to provide farmer members with high quality motor oils, blended in their own plants to meet their own definite farm use specifications. That first plant was located in Indianapolis, Indiana.

As time went on and the advantages of pooled purchasing became apparent, other farm supply products were added to the line and other cooperative wholesalers applied for membership. With the addition of other products and members, a more descriptive name seemed advisable, and so, in 1936, the present name of United Co-Operatives, Inc., was adopted.

Today this organization has a membership of 32 regional farm supply cooperatives. These members, operating in 42 states of the United States, in the Province of Ontario, Canada, and in Puerto Rico, serve some two million farmer patrons through more than six thousand retail outlets.

In 1942 the main office was moved to Alliance, Ohio, from Indianapolis, Indiana. This was done because Alliance seemed, at that time, to be closer to the geographical center of United's operations. All Unico operations today are under the direction of General Manager Merritt H. Crouch.

### United Serves Two Functions

1. *United Manufactures or Processes Farm Supplies*

A complete line of Unico interior and exterior paints is produced in the modern Alliance plant, which has an annual capacity of one million gallons. Electric fence controllers, egg cooling equipment and infrared brooders are manufactured at the Farm Mechanical Plant in Alliance. A full line of Unico farm and household chemicals, and poultry and animal health aid products is processed in the plants in Alliance and Montgomery, Alabama.

As might be expected of an organization which set out to supply the American farmer with quality oils and greases, United's petroleum


**FISKE BROTHERS REFINING CO.**

Established 1870

★

NEWARK, N. J.

TOLEDO, OHIO

★

Manufacturers of

**LUBRICATING GREASES**

department, under the supervision of G. E. Castree, now has three plants for this purpose. They are located in Indianapolis, Indiana; Newark, Delaware; and Kenton, Ohio. All three of these plants employ the most modern methods of blending, processing and packaging of petroleum products.

United's high standards of quality for its petroleum products are rigidly controlled in the modern laboratory maintained in Alliance. Here raw stocks are checked to United's own specifications before blending. In addition, samples are received from all parts of United's vast territory for laboratory testing. Thus, the quality of Unico motor oils and greases is controlled, all the way from the raw stocks to the finished products, with one objective: To produce petroleum products that will withstand the rigorous demands made of them by the farmer.

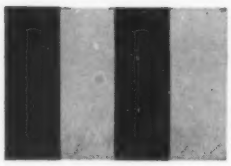
2. *United Procures Farm Supplies*

United buys for its member patrons such diversified items as: steel and aluminum roofing, wire fencing, corn cribs, grain bins, plastic pipe, poultry and livestock equipment, power mowers, garden tractors, twine, garden tools, food freezers, milk coolers and tanks, ranges, laundry equipment, water heaters, anti-freeze, tires and many hundreds of other quality farm supply products bearing the Unico trademark.

### Other Offices

A sales office is maintained in San Mateo, California, for the convenience of members in California, Oregon, Washington and Utah; and a second sales office in Memphis, Tennessee is operated in conjunction with the distribution of all types of petroleum products in the Mid-South area.

United Co-Operatives, Inc., is a bonafide agricultural cooperative, operating under the statutes of the Capper-Volstead Act of 1922, and of the Agricultural Marketing Act of the state of Indiana. It remains today, as in 1930, dedicated to the purpose of raising the standard of living for American agriculture.



# Literature and Patent Abstracts

## Composition

### Salts of Acrylamide-Acrylic Acid Ester Copolymers as Grease-Thickening Agents

According to Hotten and Lowe (U. S. Patent 2,868,728, assigned to California Research corporation) high temperature lubricating greases having improved resistance to oxidation and to emulsification in water are formed by thickening oil with an alkali metal salt of a copolymer of an ester of acrylic acid and an alpha-substituted acrylamide. The ratios of the above ester to the amide should be 3 to 1 to 6 to 1 on a mole basis.

The first step in the production of the thickener is the formation of the copolymer. For example a mixture of 152.4 grams (0.6 mole) lauryl methacrylate, 8.5 grams (0.1 mole) methacrylamide, 0.25 gram benzyl peroxide, and 75 ml. of benzene was charged to a two-liter reaction vessel. The mixture was heated, with stirring, at 170 to 180°F. for two and one-half hours while nitrogen was used to blanket the mass. The resulting copolymer was recovered by first dissolving in 300 ml. benzene and then precipitated from solution by the addition of one liter of acetone.

The next step is the formation of the alkali salt of the copolymer. Thus, 5 grams of the above copolymer, 0.25 gram of sodium hydroxide in 10 ml. of 95 per cent ethanol, and 250 ml. benzene were heated under reflux for two hours after which the solvents were removed by distillation.

Finally, the resulting sodium salt was added to 21.5 grams of a California solvent refined oil having a viscosity of 480 SUS at 100°F. The mixture was heated with stirring to a temperature of 450°F. and then milled through a three-roll mill four times and reheated to 500°F.

The final lubricating grease had an unworked ASTM penetration of 315 at 70°F. and an ASTM dropping point of 505°F. From 10 to 30 per cent of the thickener is required for the production of lubricating greases.

### Calcium Soap of an Ankenyl Substituted Succinic Acid as a Thickener for Lubricating Greases

Anhydrous calcium soap lubricating greases having high dropping points and excellent shear and water

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stability are described by Nelson and Verdol (U. S. Patent 2,868,729, assigned to Sinclair Refining Co.). Such soaps are formed from alkenyl succinic acids in which the alkenyl substituent preferably contains 18 to 35 carbon atoms. Such acids may be formed by condensing an olefin with maleic anhydride.

For example, equimolecular quantities of 1-octadecene and maleic anhydride were heated at 200 to 250°C. for sixteen hours in a flask equipped with a reflux condenser and a stirrer. This formed a crude octadecylene succinic anhydride which can be used in this form or after topping under reduced pressure to remove unreacted material.

One pound of the crude anhydride, 0.25 pound of hydrated lime, one pound of water and three pounds of a conventionally refined Coastal oil of 300 SUS at 100°F. were charged to a grease kettle and after thorough mixing heated to 170°F. At this point soap had formed and free water was present. After continued heating and stirring for twenty minutes the temperature reached 230°F. and free water had disappeared. During the following ten minutes another pound of oil was added making the soap concentration 20 per cent. The mass was then dehydrated by heating to 330°F. for ninety minutes, cooled and milled after the addition of 0.05 pound of Age Rite Resin D. The finished lubricant had a worked penetration of 234 and a dropping point of over 500°F.

### Oil Dispersible Phytates as Grease Thickeners

Salts of phytic acid are obtained from corn steep liquor or during the wet milling in the production of corn starch. Such salts can be converted to the acid if desired. Finlayson and Jordan (U. S. Patent 2,871,190, assigned to National Lead Company) suggest the use of phytic acid reacted with organic bases as a thickener for lubricating oils.

Thus, forty-four and four-tenths grams of laurylamine were converted to the acetate with acetic acid and added to a water solution of twenty-one and two-tenths grams of sodium phytate containing 11.5 per cent moisture. The reaction product was relatively insoluble in water and formed a precipitate which when dried on a steam-heated drum dryer gave a friable white waxy solid.

Twenty grams of the compound whose formation was just described were milled on a three-roll mill with 180 grams of coastal bright stock having an SUS viscosity of 1100 at 100°F. A smooth translucent lubricating grease having an unworked penetration of 395 was obtained. This product had no apparent dropping point and was resistant to the action of water.

### Lubricating Greases Stabilized with Organic Carbonates

Schott (U. S. Patent 2,871,191,


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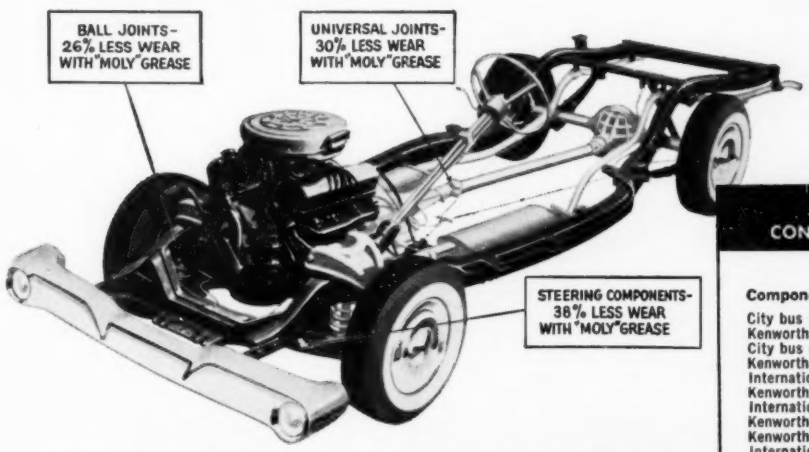
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UNIVERSAL JOINTS- 30% LESS WEAR WITH "MOLY" GREASE
STEERING COMPONENTS- 38% LESS WEAR WITH "MOLY" GREASE

In 2-year, 2,000,000-mile test, wear on critical parts lubricated with Molysulfide chassis grease was compared with wear for those lubricated with a conventional premium grease. Figures shown in the illustration are combined averages for Fords.

MOLYSULFIDE GREASE vs. CONVENTIONAL PREMIUM GREASE

TRUCKS AND BUSES

| Component | Average improvement or % less wear |
|---|---|
| City bus steering ball | 88% |
| Kenworth truck steering ball | 18% |
| City bus steering universal joint | 39% |
| Kenworth truck king pins | 57% |
| International truck king pins | 42% |
| Kenworth truck front drive line universal joint | 59% |
| International truck drive line universal joint | 32% |
| Kenworth truck front spring pin | 41% |
| Kenworth truck rear spring pin | 40% |
| International truck front spring pin | 87% |
| International truck rear spring pin | 33% |

NOTE: Figures are averages for several parts that make up entire component. Also, they are average results over all such components tested.

CLIMAX MOLYBDENUM

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assigned to Socony Mobil Oil company, Inc.) claims that the addition of 0.01 to 5 per cent of certain organic carbonates, such as di (butoxydiethylene glycol) carbonate, diphenyl carbonate, diethylene bisphenyl carbonate, butyl diglycol carbonate or lauryl carbonate, to certain alkaline earth metal soap greases will stabilize the structure.

The lubricating greases particularly mentioned are those made from a calcium soap-calcium acetate thickener. Also the presence of a small amount of glycerol is desirable in such products.

For example, a series of experimental lubricants were made, all of which contained 6.1 per cent oleic acid, 6.1 per cent stearic acid, 1.3 per cent acetic acid, and 2.8 per cent lime flour. The first lot, containing 0.14 per cent water and 83.7 per cent of a 500 at 100 oil, resulted in a separation of the thickener and oil. The next lot, having 0.7 per cent di butoxydiethylene glycol carbonate, 0.16 per cent water and 83 per cent of the 500 oil, had a penetration of 380. When the additive was either 0.25 or 1.1 per cent of glycerol, semifluid products resulted. However, when 0.25 per cent glycerol, 0.85 per cent of the carbonate and .24 per cent of water were present a lubricating grease having a penetration of 298 was formed.

The organic carbonate was added before the batch of lubricating grease was completely dehydrated and at a temperature of 300 to 310°F.

### High Dropping Point Lithium Base Lubricating Greases

According to Jordan, Dilworth and Roach (U. S. Patent 2,872,417 assigned to The Texas company) the addition of 0.5 to 5 per cent by weight of phosphite or phosphate esters to lithium base lubricating greases, containing 0.15 to 0.5 per cent by weight of excess lithium hydroxide, increases the dropping point of the product.

While no detailed formulation and processing instructions are given by the authors they state that any standard procedure can be used but preferably saponification and dehydration are carried on above the melting point of the soap followed by controlled cooling with agitation through the transition stage. The phosphorus acid ester is incorporated during the stirred cooling of the lubricating grease.

The necessity for excess base is illustrated in the case of a product thickened with lithium myristate and containing in each case 2.7 per cent of tricresyl phosphate. When the excess lithium hydroxide content was 0.01 per cent the dropping point was 414°F. Raising this excess to 0.05 per cent increased the dropping point to 430°F. and a further increase to 0.18 per cent excess lithium hydroxide raised the dropping point to over 500°F.

To indicate the proportion of ester needed a base lubricant was chosen containing 7 per cent of a


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lithium soap prepared from methyl 12-hydroxy stearate and having 0.2 per cent excess lithium hydroxide. This product had a dropping point of 372°F. but addition of 0.5 per cent of triamyl phosphite raised this to 392 to 396°F. Proportions of either 1 per cent, 2 per cent or 3 per cent of the triamyl phosphite raised the dropping point above 500°F.

In the case of a similar product which also contained 5 per cent of lead naphthenate and 7½ per cent of sulfurized sperm oil as well as 0.2 per cent excess lithium hydroxide, the dropping point was raised from 351 to 410°F. by the addition of 1½ per cent of triamyl phosphite.

Mention is made that the action described is specific to lubricating greases containing lithium soap as the sole thickening agent. In fact cases are cited where a calcium soap of 12-hydroxy stearic acid product, a mixed lithium-lead soap product, and a mixed lithium-calcium product all had dropping points lowered by the addition of triamyl phosphite.

**Water-Resistant Sodium Base Lubricating Greases**

According to Keil and Boeck, *Chemical Technology* (Berlin) 10, p. 307, 1958, the sodium soaps of long chain fatty acids, such as montanic acid, are suitable thickeners for lubricating greases and the product is stable against the action of water.

## Composition and Processing

**Anti-Friction Bearing Lubricating Greases**

Channeling type lubricating greases useful for ball bearing lubrication and which have spindle life of over 1600 hours but which are comparatively low in soap content are described by Morway (U.S. Patent 2,872,416, assigned to Esso Research and Engineering company). The particular thickener employed is a complex sodium soap obtained by the alkali fusion of rapeseed oil.

The improvement in processing consists of first forming the thick-



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| Titre | 73-75°C | 86-88°C |
| Iodine Value | 1-4 | 3 max. |
| Acid Value | 175-183 | 4 max. |
| Saponification value | 185-192 | 176-182 |
| Hydroxyl value | 154 min. | 157 min. |
| Acetyl value | | 139 min. |

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ener in a low viscosity, low V.I. oil and then kettle cooling the mass to give a lubricating grease which is then blended with a minor amount of high viscosity, high V.I. oil and homogenizing the mixture to its ultimate hardness.

For example a grease base was prepared from the following ingredients:

| | |
|---|---|
| Rapeseed oil | 29% |
| Sodium petroleum sulfonate | 0.80% |
| Sodium hydroxide | 5.92% |
| Phenyl alpha naphthylamine | 1.00% |
| Metal deactivator | 0.50% |
| Refined Coastal Crude distillate | 62.78% |

This oil had a viscosity of 500 SUS at 100°F., a V.I. of 40 and a flash point of 395°F.

The rapeseed and one-half of the mineral oil were charged to a fire heated kettle and warmed to 150°F. The sodium sulfonate was then added followed by a 40 per cent aqueous solution of the sodium hydroxide. The mass was heated to 350°F., where most of the water was removed. The balance of the mineral oil was then added, and the temperature raised to 500°F. The hot mass was then transferred to a cooling kettle and rapidly cooled to 275°F. within four hours. The inhibitors were then added and the grease base further cooled to 200°F.

Next, 50.8 per cent of this grease base was blended with 8.75 per cent of a solvent-refined, propane precipitated Mid-Continent residuum of 2200 viscosity SUS at 100°F. and 100 V.I., 39.70 per cent of a solvent-refined, Mid-Continent distillate having a viscosity of 367 SUS at 100°F. and 102 V.I., 0.50 per cent of phenyl alpha naphthylamine, and 0.25 per cent of metal deactivator. This mixture was semi-fluid but when pumped to a Gaulin homogenizer and homogenized to its ultimate hardness a lubricating grease resulted which had a worked penetration of 342, a dropping point of 481°F., oil separation of 0.8 per cent after 50 hours at 150°F. in a 60 mesh wire cone, pressure drop of five pounds in 158 hours in an oxidation test, and operated for 4,606 hours in an AFBMA-NLGI Spindle test at 250°F. and 10,000 rpm.

Other lubricating greases containing greater proportions of soap, but with all of the oil of a low V.I. type only operated 1,000 to 1,600 hours on the Spindle test. Likewise a product with a lesser amount of residuum failed in 1,800 hours.

## Process

### Manufacture of Lithium Base Lubricating Grease by Combined Oil Quench and Recycle Cooling

A method for controlled crystallization of a molten mixture of lithium 12-hydroxystearate and lubricating oil is described by Givens and Pitman (see U.S. Patent 2,876,-198, assigned to The Texas com-


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| Specific Gravity 20°C. / 20°C. | 0.940-0.960 | Fire Point | 570°F. approx. |
| Free Fatty Acid (as Oleic) | 10.0-14.0% | Saybolt Viscosity at 210°F. | 155 sec. approx. |
| Moisture | 0.5-1.2% | Iodine Value (Hanus) | 20.0-35.0 |
| Ash | 0.1% Max. | Saponification Number | 100.0-116.0 |
| Melting Point | 36.0°-44.0°C. | Penetration at 77°F. unworked | 150-180 mm/10 |
| Flash Point | 540°F. approx. | worked | 340-370 mm/10 |
| | | Color ASTM (Max.): 10% | 4.5 |
| | | 30% | Greater than #8 |

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pany). This consists of heating the soap oil mixture to 395 to 405°F. and then simultaneously quenching with 5 to 25 per cent of the total oil and recycling a relatively small proportion of the mixture through an external cooler.

The quenching step should cool the mass below 385°F. and the recycling is continued at least until the temperature is reduced to 365° F. and preferably until the mass has cooled to 300°F. A desirable rate of cooling is 3 to 15°F. per minute. Once the lubricating grease has reached the latter temperatures it can be further cooled by either circulating cooling fluid through a kettle jacket or by transferring to another vessel.

Combination of the two methods of cooling results in lower soap percentages for a given penetration than if recycle cooling alone were used. In one illustration, the fatty material used was methyl esters of 12-hydroxy stearic acid. The lithium soap of this material was dispersed in a blended oil having a viscosity SUS of 1037 at 100°F. and a V.I. of 77.6. When cooling was by recycling only a soap content of 9.18 per cent gave a finished product with a worked penetration of 268. When cooling was by both quenching and recycling, the final product had a soap content of 6.5 per cent and a worked penetration of 266.

### Open Gear Lubricants

By diluting asphaltic materials with highly aromatic lubricating oils, open gear lubricants are formed which have unusual metal-adhering properties and superior fluidity and stringiness. Such products are described by Wasson and Howell (U.S. Patent 2,876,199, assigned to Esso Research and Engineering Co.).

The mixtures described have a viscosity of 1,000 to 6,000 SUS at 210°F. and consist of a blend of 40 to 70 per cent of an asphaltic material and 60 to 30 per cent of a highly aromatic solvent extracted oil. From 0.6 to 3 per cent of a polymer of styrene and isobutylene, having a styrene content of 50 per cent, may be included in the gear lubricant.

A preferred asphalt has a viscosity of 240 to 1200 Saybolt Furol at 300°F. Desirable oils have a viscosity of 60 to 360 SUS at 210°F., a V.I. of −40 to −330 and an aniline point of 90 to 120°F.

Thus, a gear lubricant having a viscosity of 5,500 SUS at 210°F. consists of 68 per cent of a reduced and oxidized asphalt and 32 per cent of a highly aromatic phenol extract of a naphthenic distillate having a viscosity of 143 SUS at 210°F., a V.I. of −235 and an aniline point of 111°F.

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# Industry News

## Witco Granted Patent on New Grease

Witco Chemical Company, Inc., has been granted U.S. Patent 2,859,-179 covering a grease composed of lubricating oil and, as thickening agent, a metallic soap (preferably aluminum) of which the fatty acid portion is a mixture of monocarboxylic and sebacic acids.

In testing-machine performance, grease produced according to this patent shows no substantial breakdown below 100,000 strokes, as compared with the usual performance figure of 5000. In addition, it sets more quickly and remains stable at higher temperature.

Other advantages include lower soap-content requirements and greater stiffness without deterioration of grease structure.

The sebacic acid content of the metallic soap component may normally vary from five to 20 per cent. The amount of soap used depends on the grease stiffness required, but, in general, a six-per cent concentration assures satisfactory results.

The soap specified in the patent is covered by Witco Patent 2,699,-428, and licenses to produce it are available upon request.

Witco Chemical company will also license any manufacturer to use the procedures outlined in Patent 2,859,179.

Manufacturers that purchase soap made according to Patent 2,699,428 from Witco or its licensees may market the grease produced therefrom without the payment of royalties.

## Moly Lubricant Suppliers List Produced

A handy list of U.S. and Canadian suppliers of "Moly" lubricants has been published by Climax Molybdenum company, a division of American Metal Climax, Inc. This bulletin – "Molysulfide Lubricants Suppliers Listing"–serves as a guide to commercial fleet operators, industrial maintenance and production people, and others concerned with lubrication problems.

Two principal lists are contained in the bulletin–chassis grease suppliers and specialty lubricant suppliers. Each listing includes the name of the company, its address, and the brand name under which it sells "Moly" lubricants. In the case of specialty producers, a breakdown is given as to the forms of lube marketed by each–powder, grease, oil or water dispersion, bonded coating.

Copies of the new bulletin (Lu–2c) are available upon request to: Climax Molybdenum company, division of American Metal Climax, Inc., 500 Fifth Avenue, New York, New York.

## Shorter Drain Intervals

Most new car dealers feel that crankcase drain intervals should be

*Continued on page 154*

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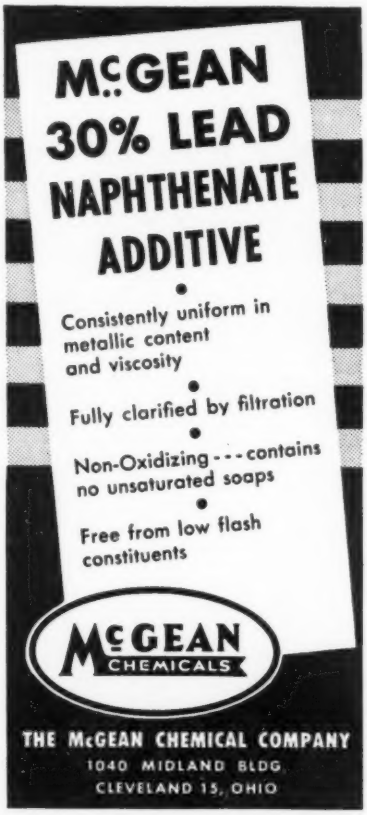

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# *"The Case for Periodic Drain-and-Refill of Axle Differential Lubricant"*

**BY MONSANTO**

A multimillion-dollar growth in your gear oil market can begin *this year* if all automotive manufacturers call for regular drain-and-refill of axle differential lubricant. To give policy makers in the automotive industry all the facts on the new, improved gear lubricants, Monsanto is publishing, consecutively, five reports which collectively build "The Case for Periodic Drain-and-Refill of Axle Differential Lubricant."

Now appearing in successive issues of *Automotive Industries*, this series of vital reports points out how the re-establishment of regular drain-and-refill practices —if taken across the automotive industry—will provide better differential lubrication in passenger cars, trucks, buses, as well as military vehicles. It emphasizes that, today, the new, improved lubricants meet the current demands for both high-speed and high-torque axle lubrication and are nationally available through service stations.

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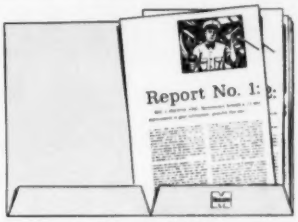


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uniform and far shorter than recommendations of leading car manufacturers, a special survey released by the division of marketing of the American Petroleum Institute said.

Of approximately 2,000 new car dealers contacted in the study, eight out of ten regarded oil changes as important items in their normal business operations. At the same time, they expressed belief that recommendations for longer drain intervals were not significant in the actual selling of new cars.

The survey, made by Crossley, S-D Surveys, Inc., New York, indicated most new car dealers would rather see a uniform oil change interval of 2,000 miles or less. Their current recommendations to new car purchasers are averaging about 1,800 miles versus manufacturers' suggestions which average about 2,800 miles.

Crossley, S-D Surveys undertook the study at the request of two marketing division groups, one under the chairmanship of Willard Wright, vice-president of Sun Oil Co., Philadelphia, Pa., and the other under the chairmanship of R. Cubicciotti, vice-president of L. Sonneborn Sons, New York. It was directed by Nicholas T. Fouriezos.


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## Molykote Lubricant Selector Chart Simplifies Choice of Proper Type

Bulletin 121, a Molykote lubricant selector chart which facilitates the choice of the proper lubricant for practically any extreme pressure lubrication job, has been just published by the Alpha-Molykote corporation.

The Selector Chart evaluates every type in the Molykote lubricant line based on temperature, environment, method of application, incorporation into common materials, and recommendations for various parts, operations and conditions.

A brief technical description of each Molykote type is also included.

Copies may be obtained from the Alpha-Molykote corporation, Stamford, Conn.

## Lincoln Publishes "Report to Management"

Application of modern centralized lubrication to reduce industrial operating costs and improve production is thoroughly discussed in "A Report to Management," new 16-page brochure published by Lincoln Engineering Co., division of the McNeil Machine and Engineering Co., St. Louis. Complimentary copies are available upon request.

The fully-illustrated booklet explains comprehensively the role of centralized lubrication—its advantages over manual methods of greasing and oiling industrial machinery; three economic areas of plant management where it can effect substantial savings; five practical steps for converting to automatic lubrication; case histories of uses in all major industries, and detailed application data on basic centralized systems.

Copies may be obtained free of charge from Lincoln Engineering Co., Industrial division, 4010 Goodfellow Blvd., St. Louis 20, Mo.

## 1958 Book of ASTM Standards

The American Society for Testing Materials has completed publication of its ten-part 1958 *Book of ASTM Standards*. This is unquestionably the society's largest publication venture and represents one of the main reasons for the society's existence. Distributed throughout the world, ASTM standards are used to cover production, purchase, and evaluation of millions of dollars worth of material annually. The size of the book has increased steadily and rapidly and will continue to grow because, as the society's technical committees' work increases, many more specifications and tests will be issued.

The increase from seven to ten parts in 1958 was necessitated by a growth in size of individual parts to the point where they could no longer be bound economically and were becoming unwieldy in size.

The statistics alone of this monumental reference work upon which American industry is so dependent for its materials requirements are impressive. Within the ten parts will be contained 2,450 standard specifications, methods of test, definitions of terms, and recommended practices. These will occupy 13,600 pages.

Each part is complete with a detailed subject index and a list of standards in numeric sequence.

To keep this book up to date, supplements will be issued to each part late in 1959 and 1960. As a service, a complete index is furnished without charge with each set. NLGI members will be interested in:

*Part 7. Petroleum Products, Lubricants, Tank Measurements, Engine Tests*, 1516 pp, 260 standards $12.00 Petroleum (fuel oils, gasoline, Stoddard solvent, diesel fuels); lubricants, grease; engine tests; measuring and sampling; tank calibration; laboratory apparatus.

# People in the Industry

## Olsen Elected President

G. A. Olsen, president of Sunland Refining corporation, was elected president of the Independent Refiners association of California last month, in Los Angeles.

A former president of NLGI (1953-54), Olsen has been on the Board of Directors since 1951 and is currently chairman of the publicity committee. Olsen is also vice-chairman of the lubrication committee, division of marketing, American Petroleum Institute.

## Fryzel Made R.I.T.A. Vice-President

Stephen T. Goode, president of R.I.T.A. Chemical Corp., 612 N. Michigan avenue, Chicago, on eve of his departure for Europe, announces the promotion of Mr. J. Fryzel, formerly sales manager, to vice-president in charge of sales. Mr. Fryzel was formerly connected with National Lead and International Harvester companies in sales capacity.

## Foote Mineral Company Promotes Two in Sales

Boyd E. Cass has been named general sales manager of Foote Mineral company, it was announced by James Fentress, director of marketing. Cass has been with the company since 1945 and previously served as manager of metallurgical sales. He is a graduate of Grove City college.

Anthony C. Demos, formerly sales engineer with Foote, has been promoted to manager of metallurgical sales. Demos joined Foote in 1948 as a research engineer and has been in metallurgical sales for the past five years. He is a graduate of the University of Virginia and received his MS degree from University of Pennsylvania in 1952.

## Chemetron Elects Howard Hartough to Head Division

Howard D. Hartough has been elected president of the chemical products division of Chemetron corporation, it was announced by Charles J. Haines, Chemetron president.

For the present, Hartough will make his headquarters in Louisville, supervising operations of the division which include Crestwood Chemical company, Dunham Chemical company, Girdler catalysts and the Holland Color and Chemical company.

Hartough has been the general manager of Girdler catalysts, Louisville. He was previously manager of marketing, chemical products division of the Houdry Process corporation, and before that was employed in various capacities at the Socony-Mobil research laboratories and the Hercules Powder company.

A native of Fairview, Ill., Hartough holds degrees in chemistry from Hope college and George Washington university. He is active in many professional and technical societies, is the author of numerous papers and holder of 75 patents.

## Atlantic Promotes Dr. A. B. Hersberger

The appointment of Dr. A. B. Hersberger to the position of general manager of the foreign marketing department, the Atlantic Refining company, has been announced by Colonel Dwight T. Colley, vice president and general manager of marketing.

In his new position, he will be responsible for the company's overall program of foreign marketing


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involving foreign crude oils, finished products, marketing subsidiaries, and further market development. Dr. Hersberger will also direct certain domestic sales activities and continue as a member of the general marketing staff.

Dr. Hersberger completed graduate and doctorate studies in chemical engineering at the University of Maryland, receiving a PhD in 1936. During his graduate work he held a teaching fellowship.

Since joining the company's research and development department in 1936, he has held many important research and marketing management posts. From 1947 to 1951, he served as manager of chemical product sales. In 1951, he became manager of the product sales division, and in 1957, manager of headquarters sales and special services department. In addition, he has served as president of Atlantic Chemicals, S.A.B. (Belgium); director, Atlantic Refining company of Brazil; and chairman of the board, Griffith-Consumers company.

Dr. Hersberger has been active in many organizations, including the American Chemical Society, Manufacturing Chemists association, and the Association of American Soap & Glycerine Producers. He has served as an officer of the University of Maryland Alumni association, and is currently a trustee of the National Petroleum association.

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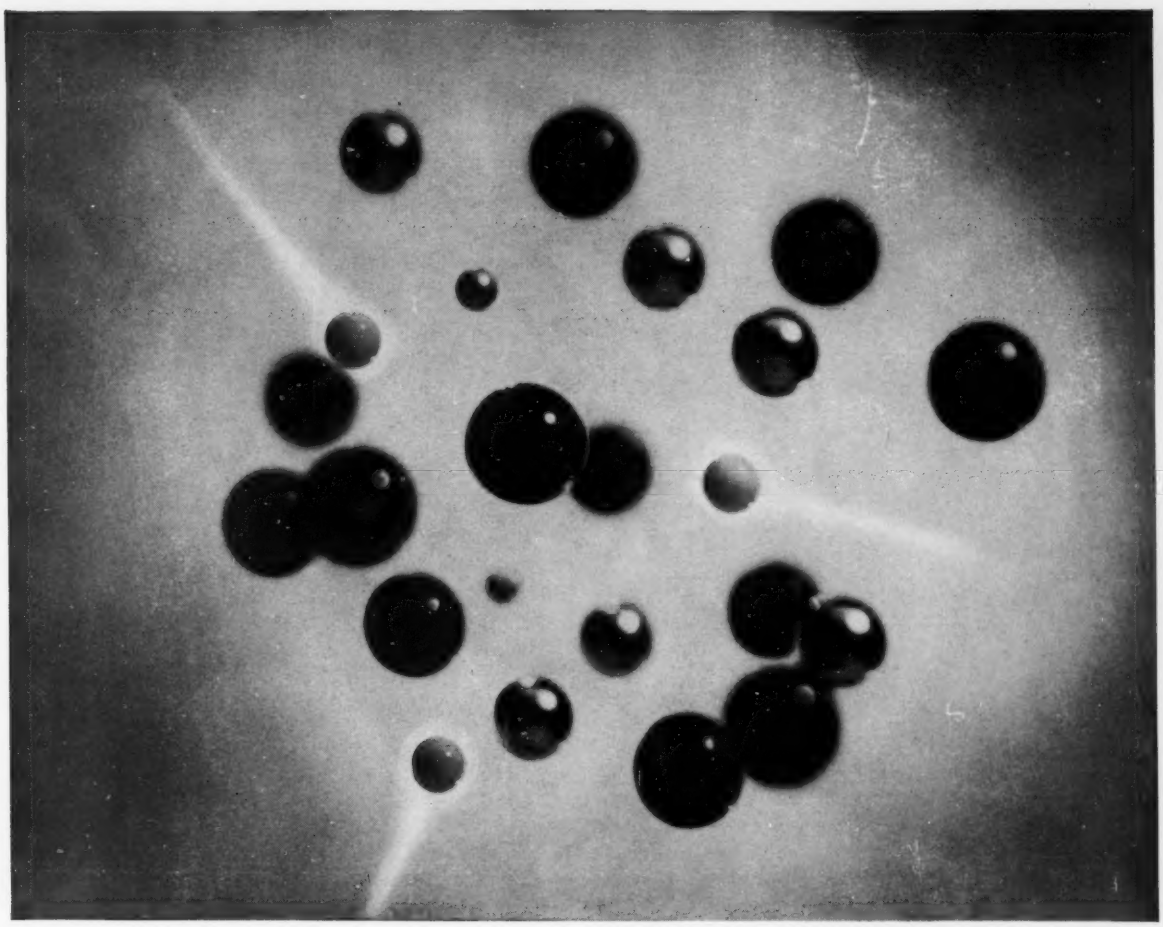

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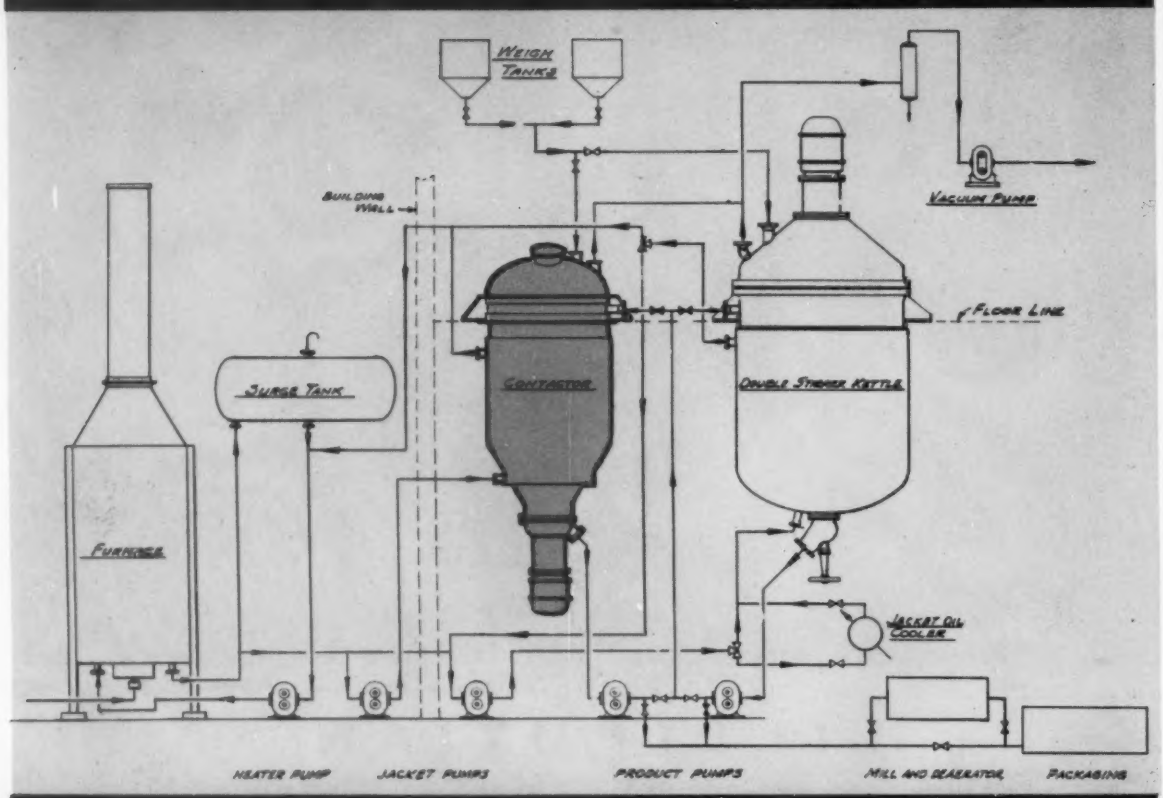


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